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X-Ray Diffraction by Gaseous Benzene Derivatives

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The Debye method for the determination of interatomic distances in single molecules is applied to ortho and para-dichlorbenzene. Results with monochlorbenzene are used to correct the scattering curves so as to isolate the Cl—Cl scattering. The resulting Cl—Cl curves show good agreement with theoretical curves constructed for distances of 3.0 and 6.25A, respectively. The measurements indicate a plane hexagonal benzene molecule with the chlorine atoms lying in or near the plane.

IT has previously been shown[1] that the positions of peaks in the x-ray scattering curves for ortho and para-dichlorbenzene agree with those in theoretical curves constructed according to Debye's theory.[2] Work of a more quantitative nature has since been in progress and the results may now be reported.

EXPERIMENTAL

A diagram of the scattering camera is shown in Fig. 1. The substance under investigation is heated in the vaporizer B to a temperature somewhat below its boiling point and the vapor carried into the scattering chamber C by a slow current of dry hydrogen. This permits vaporization at a temperature below the softening point of solder (170°) and minimizes decomposition of high boiling samples. The scattering chamber is heated about 15° above the temperature in B. X-rays passing through the slits S_1S_2 enter the scattering chamber at the front window and scattered rays pass through the upper window to the film. Both windows are sealed by thin nickel foil soldered to the brass container. That over the upper window is bent in a semicircle in order to avoid angular variation of absorption and it serves in addition as a filter for the copper radiation used. (It is essential that the filter lie between the scatterer and the film because the fluorescence of the scattering atoms would otherwise obscure interference phenomena.) The thin nickel foil is

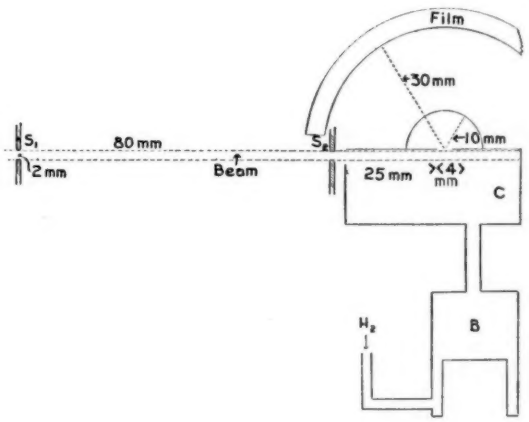

FIG. 1. Gas scattering apparatus.

[1] Pierce, Phys. Rev. **43**, 145 (1933).

[2] For a complete discussion of the theory and experimental methods see Bewilogua, Phys. Zeits. **32**, 265 (1931).

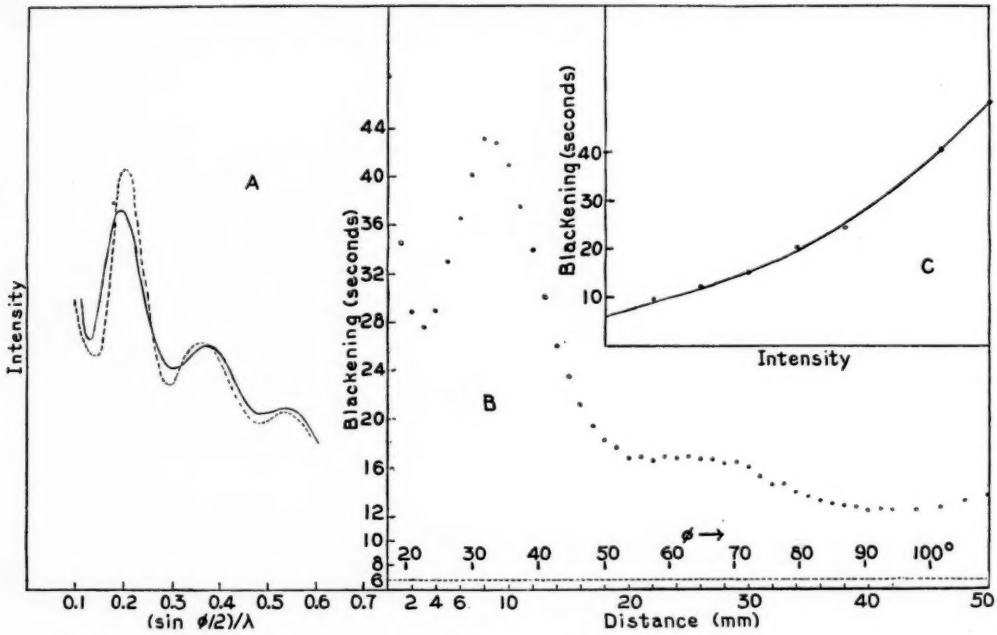

FIG. 2. A, corrected scattering of CCl_4. (Solid curve, experimental; dotted curve, Bewilogua.) B, photometer readings for a typical film. C, intensity-blackening curve for film of 2B.

prepared by electrolysis of a buffered nickel sulfate solution with a molybdenum cathode.[3]

A copper target demountable tube is used as the source of radiation. At 30 kv and 25 m.a. an exposure time of two to six hours is sufficient. The effect of general radiation is only slightly greater at this voltage than at 20 kv and the higher voltage is used because of the great gain in intensity. The relation between photographic blackening and intensity of radiation is determined separately for each film by test spots. These are made by a series of accurately timed exposures for a piece of the same film as the experiment. The two parts of the film are developed simultaneously in a tank. Radiation scattered at 90° from a copper block was used for making the test spots.

Blackening is determined by a photoelectric microphotometer, available through the courtesy of Dr. Elmer Dershem of the Department of Physics, University of Chicago. Experimental film and test spots are measured under identical conditions and a curve of blackening *vs.* intensity is constructed for the test spots. Blackening values for the experiment are then read off as intensity values from this curve. Results for a portion of a film for carbon tetrachloride are shown in Fig. 2. B gives the original photometer readings in seconds for 1 mm intervals along the film and C is the test spot curve. A shows the intensity, corrected for polarization by dividing values at each angle by $(1+\cos^2\phi)/2$, as a function of $(\sin\phi/2)/\lambda$. Bewilogua's[2] values are shown for comparison as the dotted curve. The general agreement in the position of the inflection points is good, but the intensity values are not so good as those found by Bewilogua. Considerable time was spent in attempting to improve the precision of the intensity measurements. Results were very reproducible in a given blackening range, but perfect agreement could not be obtained for films of widely different photographic blackening and the source of error was not located. This however does not greatly affect the results of the present experiments because no maxima are introduced into the scattering curve by the error. It does render the results in the vicinity of $\phi=90°$ somewhat uncertain because in making the correction for polarization the factor changes most rapidly there and slight errors in

[3] Kersten, Rev. Sci. Inst. **2**, 649 (1931).

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the intensity curve are magnified. Absence of stray scattering from the camera was proven by an experiment with hydrogen gas. At double the normal exposure time very little blackening was obtained.

Average intensity-angle curves are shown in Fig. 3 for carbon tetrachloride, monochlorbenzene, ortho and para-dichlorbenzene. All are drawn to the same scale but the zero positions are displaced as indicated.

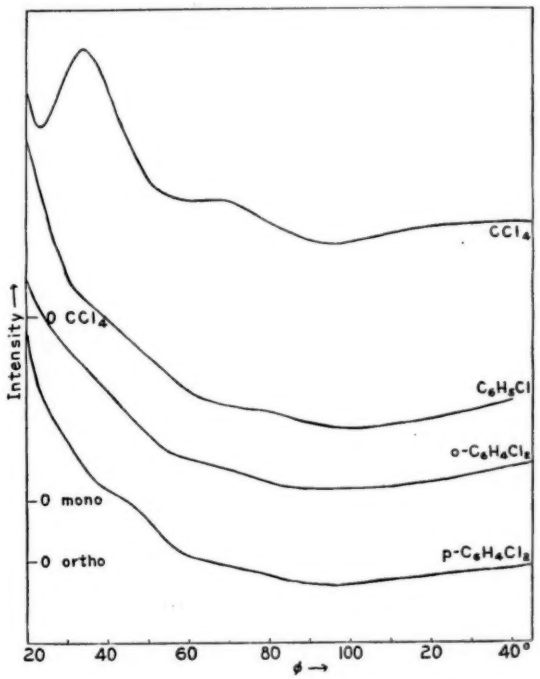

FIG. 3. Experimental intensity curves.

TREATMENT OF RESULTS

The coherent scattering of single molecules may be calculated by the Debye equation

$$I_\varphi \alpha \frac{1+\cos^2\phi}{2} \sum_1^N \sum_1^N F_i F_j \sin x_{ij}/x_{ij},$$

where $x_{ij}=(4\pi\, d_{ij} \sin\phi/2)/\lambda$, d_{ij} is the distance from the i-th to the j-th atom, F is the atomic form factor or structure factor, and $(1+\cos^2\phi)/2$ is the polarization factor. The general method for determining distances d_{ij} is to compare experimental intensity curves with theoretical curves drawn by use of the above equation but this method does not afford a simple and unique solution for such complex molecules as the dichlorbenzenes because of the large number of factors involved. This is shown in Fig. 4 which gives the theoretical intensity curve for each of the components of para-dichlorbenzene. The various scattering curves for the coherent scattering are calculated from the equations:

$$I_{C-C} = 6F_C^2\left[1+2\frac{\sin x_0}{x_0}+2\sin\frac{1.73x_0}{1.73x_0}+\frac{\sin 2x_0}{2x_0}\right];\ d_0=d_{C-C}=1.4\text{A},$$

$$I_{C-Cl} = 4F_C F_{Cl}\left[\frac{\sin x_1}{x_1}+2\sin\frac{1.54x_1}{1.54x_1}+2\sin\frac{2.27x_1}{2.27x_1}+\frac{\sin 2.55x_1}{2.55x_1}\right];\ d_1=d_{C-Cl}=1.8\text{A},$$

$$I_{Cl-Cl}=2F^2_{Cl}[1+(\sin x_2)/x_2];\ d_2=d_{Cl-Cl}=6.0\text{A}.$$

F and $(\sin x)/x$ values were obtained respectively from James and Brindley's[4] and Bauer's[5] tables. The incoherent scattering is mainly due to that of the benzene and may be calculated by the method of Heisenberg-Bewilogua.[6] The curve of Fig. 4 is the one given by Bewilogua for benzene.

Inspection of Fig. 4 shows that the scattering is largely determined by the Cl−Cl curve but it is somewhat modified by the C−C and less by the C−Cl curves. This suggests a simple method for isolating the Cl−Cl curve by subtracting from the total the C−C, C−Cl and incoherent scattering. A combined subtraction curve containing the effects of all three may be made either from the theoretical curves of Fig. 4 or experimentally from the scattering of monochlorbenzene. The latter method was thought best because fewer as-

[4] James and Brindley, Phil. Mag. **12**, 81 (1931).
[5] Bauer, J. Opt. Soc. Am. **22**, 537 (1932).
[6] Heisenberg, Phys. Zeits. **32**, 737 (1931). Bewilogua, Phys. Zeits. **32**, 740 (1931).

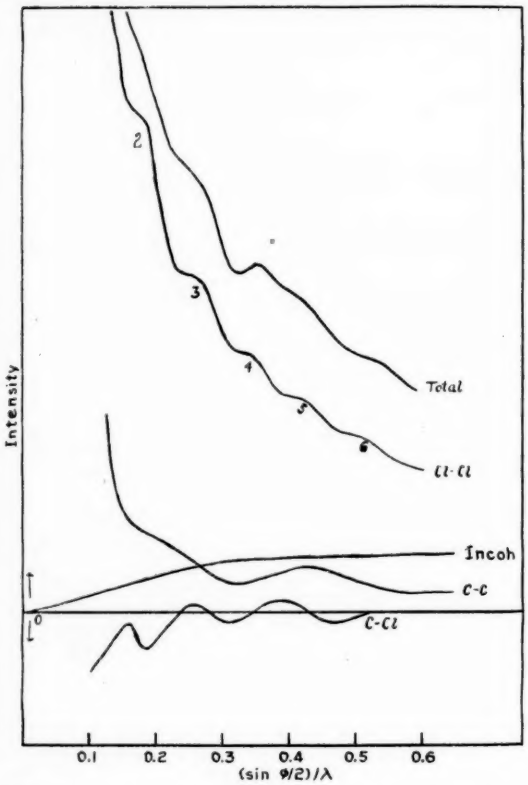

FIG. 4. Theoretical scattering of *p*-dichlorbenzene.

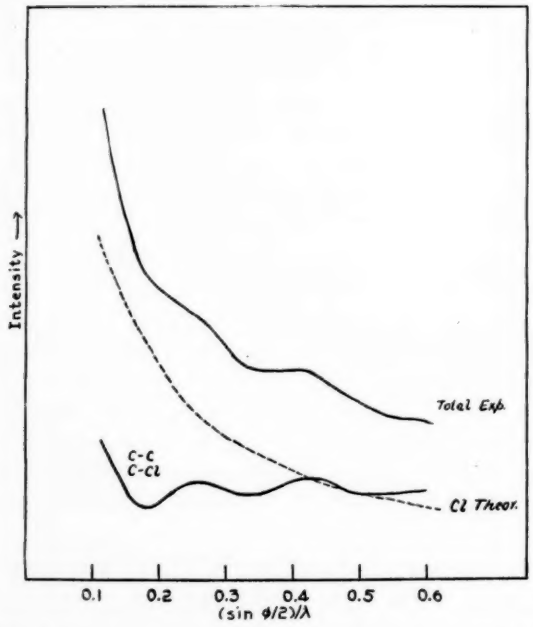

FIG. 5. Construction of correction curve from the scattering of monochlorbenzene.

sumptions are involved and the correction curve was constructed as shown in Fig. 5. Experimental scattering was determined for monochlorbenzene and the values arbitrarily equated at one point to a theoretical scattering curve similar to the one of Fig. 4. Subtraction of James and Brindley's F^2_{Cl} values from this curve leaves a correction curve containing the C−C, C−Cl and incoherent scattering. The C−Cl term occurs only one-half as much in this as in the dichlorbenzenes, but the influence of this term is so small that the discrepancy may be neglected.

Cl−Cl curves for ortho and para-dichlorbenzene are obtained by subtracting the correction curve from the respective total scattering curves. These are arbitrarily set at intensity values corresponding to the values of Fig. 4 for the theoretical para-dichlorbenzene curves. The derived Cl−Cl curves are shown as the lower curves of Fig. 6. Corresponding theoretical curves for appropriate distances are shown in the upper curves. Comparison of the two give Cl−Cl distances of 3.0 and 6.25A, respectively. Identification may be made at the first and second theoretical maxima for ortho and the second and third

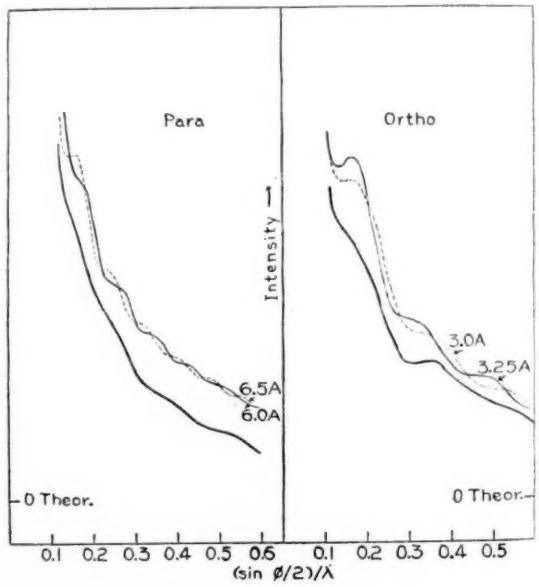

FIG. 6. Corrected Cl−Cl scattering of ortho and para-dichlorbenzene (lower curves). Theoretical Cl−Cl scattering (upper curves).

for para. The first para peak could not be experimentally determined with radiation of the wavelength used. As previously mentioned no significance can be attached to small fluctuations in the intensity curves at large angle values but the major peaks at which the comparisons are made may be recognized even in the original photometer curves before any corrections are made.

The Cl−Cl distances thus measured do not depend on any assumptions regarding the structure of the benzene molecule except that the C−C and C−Cl scattering is the same in mono- and dichlorbenzene. It is therefore only necessary to seek for a structure for benzene that will permit the Cl atoms to lie 3.0 and 6.25A apart. If C−C and C−Cl distances of 1.4 and 1.8A are assumed the measured Cl−Cl distances are best accounted for by a plane hexagonal benzene molecule with the Cl atoms lying on valence lines in or near the plane of the ring. This model gives calculated values of 3.2 and 6.4A which agree within experimental error with the values found. The result for para-dichlorbenzene is in agreement with the crystallographic measurements of Hendricks.[7] He finds that the intramolecular Cl−Cl distance in the solid compound is 6.20A.

Hendricks, Maxwell, Mosley and Jefferson[8] have recently reported measurements with electron diffraction from the di-iodobenzenes. Their results are in line with the present ones except for ortho-di-iodobenzene. They find that the ortho-iodine atoms mutually repel one another to positions about 10° from the valence angles. The precision of the present work is not as high as that obtained for the iodine compounds and it is possible that an effect of this sort might escape detection. However, since the measured value is smaller rather than larger than the calculated one it seems doubtful if this mutual repulsion exists in the chlorine compounds. The smaller value might be accounted for by a slight displacement of the Cl atoms from the plane of the ring. The general agreement in the two methods imparts confidence in the results and in their interpretations.

[7] Hendricks, Zeits. f. Krist. **84**, 85 (1932).

[8] Hendricks, Maxwell, Mosley and Jefferson, J. Chem. Phys. **1**, 549 (1933).

The Influence of Foreign Gases on the Intensity of Infrared Absorption

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Measurements have been made on the effect of helium, argon, oxygen, nitrogen, ethane, carbon dioxide and hydrogen on the maximum absorption by nitrous oxide in the region of 4.5μ, by using a spectrometer of low resolving power. Some measurements have also been made with carbon monoxide and ethyl bromide as the absorbing gases. Relative "optical" collision diameters, calculated on the postulate that the mean free paths are equal in gas mixtures having the same relative absorption coefficients, show a linear relationship with the gas-kinetic diameters as determined by viscosity measurements. The applicability of Beer's law is discussed in connection with the use of infrared absorption measurements as a means of analysis.

THE effect of foreign gases in increasing the infrared absorption of a given amount of absorbing gas was first investigated by Ångstrom.[1] von Bahr[2] extended the study with measurements which indicated that the intensity was the same function of the total pressure for all foreign gases. Hertz[3] found that there was a difference in the effects of hydrogen and air on the intensity of the absorption by carbon dioxide. The present investigation was undertaken in order to obtain a quantitative measure of the effect of various non-absorbing gases on the intensity of the maximum absorption of certain unresolved bands in the infrared.

Nitrous oxide was selected as one of the absorbing gases because the effect of foreign gases on its thermal decomposition had been investigated by Volmer and his co-workers.[4] Their results showed that there is a wide variation in the effective cross sections of the foreign gas molecules for an activation collision, and that these cross sections are not related to the gas kinetic cross sections. It seemed important to determine whether the effective cross sections of foreign gases for increasing infrared absorption are related to the effective diameters for chemical activation, or to the gas kinetic diameters, or to neither. The results show that they are related to the gas kinetic diameters.

Measurements were also made with carbon monoxide and ethyl bromide as the absorbing gases. The foreign gases were helium, argon, oxygen, nitrogen, ethane, carbon dioxide and hydrogen.

APPARATUS

A rocksalt prism spectrometer having a Wadsworth mounting of prism and plane mirror was used. The intensities were measured with a thermopile-galvanometer circuit, taking the average of several galvanometer deflections at each setting of the spectrometer table. As the galvanometer was of the Paschen type, it had the disadvantage that the deflection was not a linear function of the current from the thermopile. The amount of the deviation from linearity depended upon the sensitivity, and since the sensitivity varied from day to day, it was necessary to devise a method of calibration which was simple enough to enable its application with each set of data.

Two light sources were arranged so that they could shine either separately or simultaneously on the thermopile slit. Measurements of the deflections produced by the separate and combined sources indicated that the corrections to be added to the observed deflections to obtain values which were proportional to the intensity could be represented quite accurately by a parabolic function of the deflection. The unit of intensity was selected as one-two hundredth of a 200 mm

[1] L. Ångstrom, Ark. f. Math., Astron. och Fys. 30 (1908).

[2] E. v. Bahr, Ann. d. Physik **29**, 780 (1909); **33**, 585 (1910); Verh. d. D. Phys. Ges. **15**, 673 and 710 (1913).

[3] G. Hertz, Verh. d. D. Phys. Ges. **13**, 617 (1911).

[4] M. Volmer and H. Froehlich, Zeits. f. physik. Chemie **19**, 89 (1932). M. Volmer and H. Kummerow, Zeits. f. physik. Chemie **9**, 141 (1930).

deflection on a scale 3 meters from the galvanometer. The deflection, d, produced by the simultaneous illumination of the thermopile slit by the two lights which separately gave deflections of 200 mm was measured. Then

$$y=(400-d)(x^2-200x)/(d^2-200d),$$

where x is the observed deflection and y is the correction to be added. Plots of y as a function of x were made for a series of values of d. A determination of d was made with each set of data and the corrections taken from the appropriate curve. Readings taken with various combinations of intensity of the two light sources showed that the deviations of the corrected values from linearity were of the same order of magnitude as the deviations due to the experimental error in the reading of the galvanometer deflections. The corresponding error in the transmission is less than one percent under the experimental conditions employed.

The absorption cell was in two compartments, 2 cm and 18 cm in length. The transmission was first measured with a certain pressure of gas in the 2 cm compartment, then with one-tenth the original pressure in the entire cell. Following this determination, transmissions were measured after the addition of various amounts of foreign gas. Thus in all cases the number of absorbing molecules (or the path length, $x=$ length of cell in centimeters $\times$ pressure of gas in atmospheres, at a specified temperature) was constant and the observed variations in the absorption were functions of the environment of the absorbing molecules. It was found best to work with pressures such that the transmission was between 20 percent and 60 percent. The path lengths employed were 0.526 cm atm. for the N_2O band at 4.5μ and 2.63 cm atm. for the CO band at 4.66μ, ($T=298°K$). Under these conditions the enhancement produced in the absorption by the addition of a foreign gas was sufficient to enable its quantitative determination. Measurement of the transmissions of the compressed gas in the 2 cm compartment was omitted in the carbon monoxide experiments since the cell was not constructed to withstand pressures greater than one atmosphere.

TABLE I. *Relative absorption coefficients.*

Foreign gas	*Total pressure (mm of mercury)* N_2O (partial pressure = 20 mm)					CO (partial pressure = 100 mm)		
	50	100	200	400	700	200	400	700
He	1.39	1.87	2.44	3.06	3.56	1.32	1.74	2.21
A	1.41	1.86	2.44					
O_2	1.42	1.87	2.47	3.13	3.58	1.32	1.77	2.23
N_2	1.44	1.93	2.56			1.36	1.85	2.39
C_2H_6	1.48	2.03	2.69			1.41	1.91	2.52
(N_2O)			2.8					
CO_2	1.53	2.07	2.87					
H_2	1.57	2.19	2.91	3.53	3.85	1.45	2.01	2.59

EXPERIMENTAL RESULTS

The results are given in Table I. The "relative absorption coefficient" is the ratio of the observed absorption coefficient as calculated by Eq. (2) to that of the pure absorbing gas before the addition of the foreign gas. Most of the added gases were transparent but corrections were applied for the slight absorptions of carbon dioxide and ethane in the regions being investigated. The value 2.8 for N_2O is the ratio of the observed absorption coefficient for N_2O at 200 mm pressure in the 2 cm cell to the coefficient for N_2O at 20 mm pressure in the 20 cm cell.

The effect of the various gases on the absorption of nitrous oxide is shown graphically in Fig. 1.

Additional experiments were carried out on gaseous ethyl bromide. In no case did the addition of a transparent foreign gas affect the infrared absorption by ethyl bromide. The measurements were carried down to 10 mm of ethyl bromide, and one atmosphere of the foreign gas.

DISCUSSION

If α_ν is the absorption coefficient for light of frequency ν, the intensity I_ν of the light of this frequency which is transmitted through l cm of the absorbing gas at a pressure of p mm of mercury is given by the relation

$$I_\nu=I_\nu^0 e^{-\alpha_\nu lp},$$

where I_ν^0 is the incident intensity of the light of frequency ν. It is assumed throughout this discussion that the temperature is not varied.

In actual practice, measurements of transmission are always made on a range of frequencies from ν to $\nu+\Delta\nu$, and T, the fraction of the energy transmitted, becomes

$$T=\int_\nu^{\nu+\Delta\nu} I_\nu^0 e^{-\alpha_\nu lp}d\nu \Big/ \int_\nu^{\nu+\Delta\nu} I_\nu^0 d\nu. \qquad (1)$$

It can readily be seen from this formula that the apparent absorption coefficient α' as determined from the experimental measurements of T,

$$\alpha' = (1/lp) \cdot \ln (1/T) \qquad (2)$$

will not be a constant unless α_ν is independent of lp and has the same value for all frequencies from ν to $\nu+\Delta\nu$. Many infrared bands possess a fine structure of such separation that α_ν varies over a wide range between the frequencies ν and $\nu+\Delta\nu$, and thus one would expect deviations from Beer's law as the product lp is varied. Furthermore, the values of α' will vary with p even though the product lp is held constant because the nature of the function $\alpha_\nu = f(\nu)$ depends upon the pressure. The absence of a pressure effect on the ethyl bromide bands may be attributed to the fact that their fine structure components overlap so much that α_ν is nearly constant over small frequency ranges.

Dennison[5] has been quite successful in explaining experimentally observed absorption intensities on the assumption that the nature of $\alpha_\nu = f(\nu)$ is determined essentially by the limitation of the length of the wave trains which may be absorbed by the molecules. This limitation is caused by the approach of another molecule to a distance sufficiently close to alter the phase of the absorbing molecule. The effective diameter of a molecule for this type of collision was found to be larger than the gas kinetic diameter, but is of the same order of magnitude.[6]

Let D_{AX}, D_{AY} and D_{AN_2} represent the distance between the centers of the molecule of absorbing gas, A, and the foreign gas molecules X, Y and N_2, respectively, at which a change in phase of the absorbing molecule is effected. Making the postulate that the mean free path of the absorbing molecule is the same in all gas mixtures which have the same relative absorption coefficient, one may readily calculate the ratio D_{AX}/D_{AY} from the experimental data. The equation for the mean free path, Λ, of the absorbing gas molecule is

$$1/\Lambda = (2)^{\frac{1}{2}}\pi n_A D^2_{AA} + \pi n_X D^2_{AX}[(m_A+m_X)/m_X]^{\frac{1}{2}} \qquad (3)$$

where D_{AA} is the "optical" diameter of the N_2O molecule, the n's are the number of the molecules per cc, and the m's are their masses. Equating the mean free paths in two systems having equal relative absorption coefficients, one obtains the ratio

$$D_{AX}/D_{AY} = (n_Y/n_X)^{\frac{1}{2}}[m_X(m_A+m_Y)/m_Y(m_A+m_X)]^{\frac{1}{2}} = (p_Y/p_X)^{\frac{1}{2}}[M_X(M_A+M_Y)/M_Y(M_A+M_X)]^{\frac{1}{2}}, \qquad (4)$$

where p_X and p_Y are the equivalent partial pressures of the foreign gases as obtained from the intercepts of horizontal lines with the respective curves of plots such as shown in Fig. 1, and M_X and M_Y are the molecular weights. Ratios obtained with the use of Eq. (4) are given in the second and third columns of Table II. The effective distances of approach of the foreign gases are referred to that of nitrogen. The values given

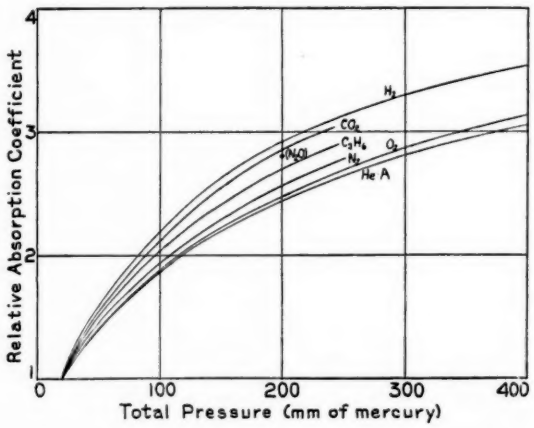

FIG. 1. Influence of pressure on relative absorption coefficients at 4.50μ of nitrous oxide (partial pressure = 20 mm).

TABLE II. *Collision diameter ratios.*

X	D_{AX}/D_{AN_2} $A=N_2O$	$A=CO$	$D_{XX}/D_{N_2N_2}$ Optical	Viscosity
He	0.63	0.64	0.07	0.62
H_2	0.70	0.68	0.24	0.70
O_2	0.97	0.95	0.93	0.97
A	0.98		0.95	0.96
N_2	1.00	1.00	1.00	1.00
C_2H_6	1.09	1.07	1.23	
N_2O	1.21		1.53	1.22
CO_2	1.23		1.58	1.20

[5] D. M. Dennison, Phys. Rev. **31**, 503 (1928).

[6] For a general discussion of the breadth of spectral lines see V. Weisskopf, Phys. Zeits. **34**, 1 (1933).

are averages of the values obtained from the equivalent pressures at the relative absorption coefficients 2.8 and 2.32 on the N_2O curves and 2.3 and 1.9 on the CO curves. All the separate values are within 0.01 of the average.

Let D_{N_2O}, D_{N_2}, etc., represent the optical collision radii. Then the data on the effect of nitrogen and nitrous oxide itself on the absorption coefficient of nitrous oxide show that $2D_{N_2O}=1.21D_{N_2O}+1.21D_{N_2}$ or $0.79D_{N_2O}=1.21D_{N_2}$ whence, $D_{N_2O,\,N_2O}/D_{N_2,\,N_2}=1.53$. The ratios of the optical diameters of the various gases to that of nitrogen are given in column 4 of Table II. The corresponding ratios of the molecular diameters obtained from viscosity measurements are given in the last column for comparison.[7]

The ratios in the last two columns are plotted against each other in Fig. 2. There appears to be a

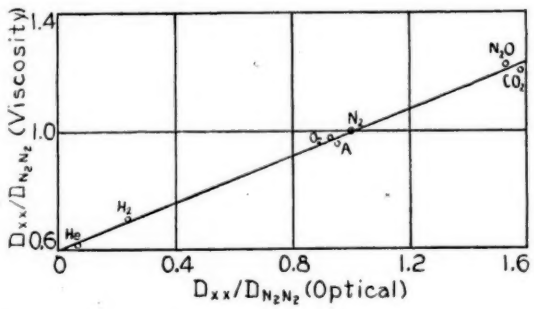

FIG. 2. Relation between "optical" diameters and gas-kinetic diameters.

linear relationship between the two types of effective diameters even though the optical diameters vary over a much wider range than do the viscosity diameters. The points are all as close to the line as can be expected from the accuracy in the determination of either type of ratio. Similar data on larger molecules and on molecules possessing electric moments are necessary to fully establish this relationship but it is unlikely that agreement with a linear relationship involving so many gases can be fortuitous. The same fundamental molecular property may determine both of the effective diameters.[8]

From measurements of the absorption of mixtures of carbon monoxide and air at a total pressure of one atmosphere and very low partial pressures of carbon monoxide, Matheson[9] found $D_{CO\,Air}$ to be 5.5A. If this value is assumed for the diameter of the N_2 molecule, the provisional values shown in Table III are obtained for the optical diameters.[10]

TABLE III. *Optical collision diameters (Angstroms).*

He	0.4	N_2	5.5
H_2	1.4	C_2H_6	6.8
O_2	5.1	N_2O	8.4
A	5.2	CO_2	8.7

Sufficient data on other absorbing gases are not available to determine whether or not these diameters are the same for all systems. It also remains to be seen whether or not the same values are obtained from the variation of absorption intensity with temperature.

Approximate effective collision diameters for the thermal activation or deactivation of nitrous oxide by foreign gases may be deduced from their effect upon the decomposition rate of nitrous oxide. These diameters also vary over a wide

[7] L. B. Loeb, *The Kinetic Theory of Gases*, p. 529, McGraw-Hill Book Co., New York (1927).

[8] Attention may also be called to the apparent agreement between the ratios $D_{AX}D_{AN_2}$ from spectroscopic data and D_X/D_{N_2} from viscosity data. If such agreement should be substantiated by further data on systems such as those just mentioned, it would seem to imply that the contribution of the absorbing molecule A to the effective distance of approach in the spectroscopic process may be small in comparison with the contribution of the perturbing molecule, which latter is proportional to the viscosity diameter. This would be quite inconsistent with the present theories of the nature of the process. Additional confirmation of this unusual circumstance would appear to be present in the fact that D_{COHe}/D_{CON_2} and D_{COH_2}/D_{CON_2} are much greater than the values calculated from the absolute values for the diameters as given in Table III (assuming $D_{CO}=5.5$ Angstroms.) More detailed experiments on carbon monoxide would be desirable to establish these values since the measurements on carbon monoxide reported here were not made under the most favorable conditions. If these values are substantiated it may mean that the optical diameters are different in different systems.

[9] L. A. Matheson, Phys. Rev. **40**, 813 (1932).

[10] Since D_{O_2}/D_{N_2} is nearly 1, Matheson's data may be used for D_{CON_2}. This may then be taken as the diameter of the nitrogen molecule because of the isosterism of nitrogen and carbon monoxide. Absolute values of the optical diameters could have been calculated by a more accurate method based on the fine structure data, but the experimental data are not sufficiently accurate to justify such an elaborate method.

range, but there does not appear to be any relation between them and the optical or viscosity diameters. The chemical activation process is much more violent than the optical effect or the viscosity effect. It is quite possible then that the latter effects should be dependent on the size of the foreign gas molecules whereas the chemical activation might be quite specific.

The influence of transparent, foreign gases on the absorption spectra is of practical importance as well as theoretical interest, in the application of Beer's law to the analysis of mixtures. Colorimetric methods for analysis, which have been successful in the visible, have been used only to a slight extent in the infrared.[11] The experimental technique is more difficult and more specialized but measurements of the intensity of infrared absorption should find application in analyzing mixtures, and in determining equilibrium constants and reaction rates, provided that Beer's logarithmic relation between intensity of light and concentration can be relied on. When the absorbing gas shows fine structure the addition of the same or another gas broadens the fine-structure lines and increases the absorption of a beam of light in such a way as to invalidate the applicability of Beer's law. If the fine structure has been completely blurred out by many collisions or if the molecule is so complex as to have no fine structure the addition of further gas has no effect, and Beer's law can be applied. The data of the present investigation and those of von Bahr[2] show that Beer's law is applicable to the infrared absorption spectra of complex substances of high molecular weight but that it is applicable to simple diatomic and triatomic gases only when the total pressure is sufficiently great.

The authors are glad to acknowledge the generous support of the Wisconsin Alumni Research Foundation during this investigation.

[11] Warburg and Leithauser, Ann. d. Physik **28**, 315 (1909), used infrared absorption measurements successfully in the analysis of mixtures of the nitrogen oxides.

On the Symmetric States of Atomic Configurations

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In the secular equations used by Eyring and his school the equations are of high order in general. When cognizance is taken of the symmetry of the configuration considered the secular equation may factor considerably. It is to be expected that the wave function for the lowest state will be invariant under the group which expresses the symmetry of the atomic configuration. This expectation is fulfilled in all cases considered. A general method is set forth upon which a derivation of such symmetric states may be carried out, and the reduced secular equation obtained. Several interesting applications of this method are carried through, including the case of eight identical orbits, centered at the corners of a cube, and eight orbits possessing tetrahedral symmetry, as in methane. The vector model is discussed and applied to the cases considered.

§1. INTRODUCTION

THE problem of determining the lowest electronic energy-states associated with a given arrangement of atomic nuclei is of considerable importance for purposes of calculating the binding and activation energies of molecules and crystal nuclei. On the basis afforded by Slater's[1] development for the construction of approximate wave functions, with which this paper is solely concerned,[2] such calculations have been carried out in a number of cases.[3]

In all such work attention is focussed upon a number, say n, of electrons between which interactions are considered, and all others, for example electrons in closed shells or valence electrons involved in bonds that are not appreciably altered by changes in the variable parameters met with in the problem, are neglected. Moreover, all terms which arise from spin in the Hamiltonian operator, describing the interactions of these n electrons, are generally neglected so that spin degeneracy is incurred. Under these conditions the Slater eigenfunctions for the n electrons are of the forms

$$\frac{1}{(n!)^{\frac{1}{2}}}\begin{vmatrix} a\zeta_a(1) & b\zeta_b(1) & \cdots & l\zeta_l(1) \\ a\zeta_a(2) & \cdots & \cdots & \cdots \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ a\zeta_a(n) & \cdots & \cdots & l\zeta_l(n) \end{vmatrix} \tag{1}$$

where a, b . . . 1 are n one-electron atomic orbital eigenfunctions which depend only upon the space variables and refer to the same or to different atoms. ζ_a is the Kronecker delta-function $\delta(m_s^a, \sigma_i)$, where σ_i is the spin variable of the ith electron, and $m_s^a = +\frac{1}{2}$ or $-\frac{1}{2}$ refers to the z component of spin momentum and the integer in parenthesis refers to the electron of whose variables the product $g\zeta_g$ is a function. In the following we shall also refer to $\delta(\frac{1}{2}, \sigma_i)$ as $\alpha(i)$ and $\delta(-\frac{1}{2}, \sigma_i)$ as $\beta(i)$. These eigenfunctions are clearly eigenfunctions of the operator S_z corresponding to the z component of total spin momentum, and although $\mathbf{S}^2$, the operator corresponding to the squared magnitude of the total spin momentum vector is not diagonal for this representation a simple method of specifying the proper linear combinations has been given by Slater[1] and more generally by Eyring and Kimball,[4] and leads to the concept of bond eigenfunctions, arising as follows:

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[1] Slater, Phys. Rev. **38**, 1109 (1931).

[2] There are several other viewpoints from which qualitative investigations of similar problems have been made. Most notable are those of Hund, Mulliken and Van Vleck.

[3] Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932). Kimball and Eyring, ibid. **54**, 3876 (1932). Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933). Pauling and Wheland, ibid. **1**, 362 (1933). Pauling and Sherman, ibid. **1**, 606 (1933).

[4] Eyring and Kimball, J. Chem. Phys. **1**, 239 (1933).

If we consider the entire set of $(n+1)n!$ functions derived from (1) by taking all possible arrangements of columns of α and β these may be divided into $n+1$ sets in each of which functions possessing an equal number of α's and β's are gathered so that each set may be assigned a definite value of S_z. In the set corresponding to $k\alpha$'s there will clearly be $n!/k!(n-k)!$ different[5] Slater functions, all of which shall be assumed to be linearly independent. Now to form an electron pair bond, electrons with antiparallel spins must be present, whence the bond-forming possibilities within any given set are the same for all functions, and the largest number of possible bonds is the smaller of the two quantities k and $n-k$. In any one set a bond function associated with the bonds a–b, c–d $\cdots$ g–h and a preassigned value of S_z is given by the sum

$$\sum \delta_{ab}(j)\delta_{cd}(j)\cdots\delta_{gh}(j)\psi_j,$$

where j ranges over all Slater functions in the set and $\delta_{rs}(j)$ is a function which is 1 if $\zeta_r(j)=\alpha$, $\zeta_s(j)=\beta$, is -1 if $\zeta_r(j)=\beta$ and $\zeta_s(j)=\alpha$, and is zero otherwise.

These functions possess the important property that $\mathbf{S}^2$ is diagonal with respect to them and different values of $S(S+1)$ are associated with functions corresponding to different numbers of bonds so that the matrix components in the Hamiltonian for the system connecting two of these is zero. In particular, the set corresponding to the maximum number of bonds corresponds to the lowest value of S, that is, the state of lowest multiplicity, and since we may generally select n to be even by augmenting each odd case with an electron at infinity, this will be a singlet state.

In practically all problems met with the state of lowest energy is a singlet so that we need only be concerned with the secular determinant corresponding to $S=0$. For even n the dimensionality of this will be

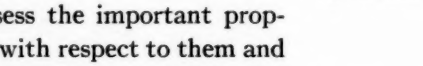
$$\frac{n!}{\left[\left(\frac{n}{2}\right)!\right]^2}-\frac{n!}{\left(n+1-\frac{n}{2}\right)\left(n-1-\frac{n}{2}\right)!}=\frac{n!}{\left(\frac{n}{2}\right)!\left(\frac{n}{2}+1\right)!},$$

so that only this number of the

$$(n-1)(n-3)(n-5)\cdots 1=n!/2^{n/2}(n/2)!$$

possible singlet bond functions are linearly independent. There are obviously many ways in which the proper number of independent bond functions may be chosen but for our purposes that so-called canonical set of Rumer[6] will be of principal interest in view of the additional developments of Pauling.[7]

It was found by Rumer that if the n orbits are arranged at the corners of an n-sided polygon the $n!2^{n/2}(n/2)!$ bond functions corresponding to a non-crossing bond pattern form an independent set,—the so-called canonical one. Moreover, any non-canonical bond eigenfunction may be resolved into a linear combination of canonical ones by successive application of the rule that



(2)

Simple rules for writing matrix components between bond eigenfunctions have been given by both Pauling[7] and Eyring and Kimball.[8]

In addition to the fact that the lowest energy level is found in the secular determinant corresponding to $S=0$ it is also to be expected on general grounds that the lowest state will be invariant under the group which expresses the symmetry of the atomic configuration. The basis for this expectation lies in the fact that symmetric states generally possess a lower mean value of kinetic energy for all electrons than other states, and as the mean value of potential energy does not differ greatly for neighboring states the total energy will be lowest for symmetric states. Hence for the purposes of the

[5] Assuming that none of the orbital functions are present more than once. This assumption does not appreciably affect the generality of the following discussion.

[6] Rumer, Nachr. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse, 337 (1932).

[7] Pauling, J. Chem. Phys. **1**, 280 (1933).

[8] Eyring and Kimball, J. Chem. Phys. **1**, 626 (1933).

aforementioned applications it is necessary to consider only that part of the secular determinant associated with symmetric states. The purpose of this article is to set forth a general method upon which a derivation of such symmetric states may be carried out. Several interesting applications of this method will be carried through.[9]

§2. Theoretical Developments

The ideal basis upon which to found a discussion of the symmetry properties of functions consists in geometrizing the functions associated with our problem. Thus, with the $n!/2^{n/2}(n/2)!$ canonical bond functions, B_i, we associate a $n!/2^{n/2}(n/2)!$ dimensional *bond-space* which may be regarded as being spanned by this system of linearly independent coordinate vectors. In general, these bond eigenfunctions will not be mutually orthogonal so that the coordinate system is not a unitary one. To each symmetry element $\mathfrak{d}^{(q)}$ of the group describing the symmetry of the atomic configuration under discussion it will be shown that there corresponds a representative matrix $\Delta^{(q)}$ in bond-space. Hence to each transformation

$$\mathfrak{d}^{(q)} \cdot \mathbf{x} = \mathbf{x}', \tag{3}$$

where $\mathbf{x}$ is a vector in ordinary space and $\mathfrak{d}^{(q)}$ is a symmetry operator, there corresponds the equation

$$\Delta^{(q)}\psi = \psi',$$

where ψ is a vector in bond-space. In particular, if ψ is expressed in terms of canonical vectors so that

$$\psi = \sum_i a_i B_i, \tag{4}$$

where the a's are constants and the summation extends over all i then

$$\begin{aligned} \Delta^{(q)}\psi &= \sum_i a_i \Delta^{(q)} B_i \\ &\quad \sum_i a_i \sum_j \alpha_{ji}^{(q)} B_j \\ &= \sum_j \Big(\sum_i \Delta_{ji}^{(q)} a_i\Big) B_j \\ &= \sum_j a_j' B_j, \end{aligned} \tag{5}$$

so that

$$a_j' = \sum_i \Delta_{ji}^{(q)} a_i, \tag{6}$$

where $\Delta_{ji}^{(q)}$ is a representation of $\mathfrak{d}^{(q)}$. For the purposes of the present discussion, we are not interested in all of bond-space but only in that part which is spanned by the complete system of vectors satisfying the relation

$$\Delta^{(q)}\psi = \psi, \tag{7}$$

where q runs through all elements of the group, —that is, in the invariant sub-space associated with the symmetry group. Since the representations of any group may be easily found for a canonical coordinate system by use of the rule (2) the determination of the sub-space may be found directly by solving the equations

$$a_j = \sum_i \Delta_{ji}^{(q)} a_i. \tag{8}$$

In actual practice we need only be concerned with the generating elements of the group since any vector which is invariant under these will be invariant under the entire group.

Concerning the construction of the representation of a given symmetry operation, this may be easily carried out if each operation, which corresponds to a rearrangement of orbits, sends canonical functions into bond functions, for if this is true the elements in the column associated with each bond function in the representation of a given operator are just the coefficients of the canonical functions when the equivalent bond-function is resolved in terms of the canonical set. It is easily shown, however, that the required condition is satisfied. For example, if $a\ b\ c\ \ldots\ 1$ is a normal arrangement of orbit-columns as shown in (1), which arrangement will appear in all Slater functions occurring in a given bond-function, and a given symmetry operation is carried out, these columns will undergo a permutation. All determinants will be brought back to the normal form by the same number of permutations of their columns, which will introduce a factor $(-1)^p$ where p is the order of the required permutation. This is equivalent to a rearrangement of electron-orbit columns accompanied by a possible change of sign. Because each of the electron-function columns in the different Slater functions comprising a given bond function

[9] Mulliken, J. Chem. Phys. **1**, 492 (1933), considers symmetric states for the purposes of his viewpoint. His methods of arriving at these are, however, essentially different from those used in this paper.

are permuted in exactly the same way, the new function, to within a sign, is the bond function corresponding to the rearrangement of bonds induced in a bond pattern by the symmetry operation.

Although the states of lowest multiplicity are kept uppermost in this discussion, the foregoing development is by no means restricted so as to be applicable to these alone, but is as general as the concept of bond-eigenfunctions.[10]

With these facts at our disposal we may now proceed with the construction of the group-representations and the solving of the equations (8) in particular cases.[11]

§3. Applications

(1) Polygonal configurations

The simplest non-trivial examples of the use of the foregoing theory occurs when the configuration of orbits under consideration form a ring structure possessing the symmetry of one of the dihedral groups D_n (i.e., the symmetry of a plane polygon). In the case for which n is even, which is the only interesting one since, for example, it corresponds to the six free orbits of C_6H_6 or the eight free electrons of C_8H_8, the group may be generated by a rotation of angle $2\pi/n$ about the axis of symmetry and a reflecting plane passing through diametrically situated centers. The Rumer polygon in this case may be selected to coincide with the structure polygon so that the manner in which the symmetry operators affect the bonds will be closely connected with the manner in which the orbits are rearranged by the same operators. Since the case $n=6$ is a typical example and is also of particular interest we shall consider it in detail. The five canonical bond patterns for this problem are illustrated in Fig. 1, where the arrowhead

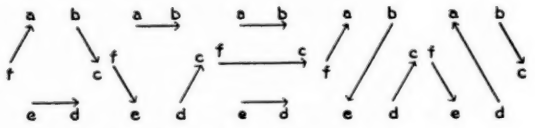


FIG. 1. Canonical bond eigenfunctions for 6 electrons.

marks the electron with spin α and the tail that with spin β. A simple rotation through an angle $\pi/3$ corresponds to an odd permutation of orbits, whence the resultant bond function in any one case is the negative of that obtained by rotating the bond pattern. The reversal of the direction of one arrow in the bond pattern is equivalent to changing the sign of the associated function so it follows at once that B_{I} is sent into B_{II}, and B_{II} into B_{I}. Similarly B_{III} is sent into B_{IV}, B_{IV} into B_{V} and B_{V} into B_{III}. On the other hand, a reflection in a line passing through fc corresponds to an even permutation so that under this operation B_{I} and B_{II} are interchanged, B_{III} is sent into itself, while B_{IV} and B_{V} are also interchanged. From these properties it is clear without further investigation that the invariant subspace in this five dimensional bond-space is two dimensional and is spanned by all vectors of the form

$$\Phi=a(B_{\mathrm{I}}+B_{\mathrm{II}})+b(B_{\mathrm{III}}+B_{\mathrm{IV}}+B_{\mathrm{V}}), \qquad (9)$$

where a and b are arbitrary to within normalization. The secular equation in terms of the two functions $B_{\mathrm{I}}+B_{\mathrm{II}}$, and $B_{\mathrm{III}}+B_{\mathrm{IV}}+B_{\mathrm{V}}$ is, after simplification[12]

$$\begin{vmatrix} Q-4\alpha+\gamma-E & 2(\alpha-\gamma) \\ 2(\alpha-\gamma) & Q+2\alpha-6\beta+\gamma-E \end{vmatrix}=0, \qquad (10)$$

[10] Eyring, Frost and Turkevich in a forthcoming paper have treated several cases for all possible multiplicities, but from a somewhat different viewpoint. We are indebted to them for the opportunity of seeing their manuscript.

[11] A general and straightforward method of obtaining the functions going with all of the representations is had by making use of the equation

$$(h/l_j)\psi_k{}^j=\Sigma_R \mathfrak{D}_{kk}{}^{(j)}(R)\mathbf{P}_R F$$

(see E. Wigner, *Gruppentheorie*, 1931, page 123, Eq. (6)) in which ψ_k belongs to the kth row of the jth irreducible representation of dimensionality l_j, whose elements are $\mathfrak{D}_{ik}{}^{(j)}(R)$, R runs through all h elements of the group. $\mathbf{P}_R$ is the operator associated with R and F is an arbitrary function. The representations are assumed known or may be derived by reduction of the generating elements of the group in a spherical harmonic coordinate system under the guiding knowledge afforded by Bethe's work (Ann. d. Physik 3, 133 (1929)).

[12] This corresponds to the usual procedure where overlap terms and multiple exchanges are neglected. In the following we shall evaluate coulombic and exchange integrals empirically by the use of Morse P.E. curves for pairs of electrons on different atoms (H. Eyring, Naturwiss. 18, 915 (1930).

where Q is the coulombic energy for the system and α, β and γ are the interchange integrals between a and b, a and c, and a and d, respectively.

Solving Eq. (10) algebraically we find

$$E=Q-\alpha-3\beta+\gamma \pm(13\alpha^2+9\beta^2+4\gamma^2-18\alpha\beta-8\alpha\gamma)^{\frac{1}{2}}. \quad (11)$$

The lowest of the two possible values corresponds to the + sign in (11). Using $Q=78.7$, $\alpha=64.8$, $\beta=12.9$, and $\gamma=5.8$ kg cal. gives $E=176.4$ kg cal. That this is actually the lowest possible eigenvalue associated with these values of α, β and γ was shown by a direct investigation of the 5th order secular equation. The values of a and b in (9) are found to be 0.450 and 0.147, respectively, for Φ normalized to 1. Thus the expectation that the lowest state is symmetric is fully borne out.

(2) Eight identical orbits centered at the corners of a cube

For the configuration consisting of eight identical orbits situated at the corners of a cube the symmetry group is O^h and possesses 48 elements. It may be generated, however, by a 3-fold axis passing through C of Fig. 2, a 4-fold axis passing orthogonally through the center of the square *cdef*, and an inversion at the center of the cube. There are 14 canonical bond eigenfunctions in this case, illustrated in Fig. 3.

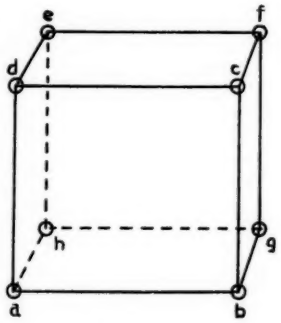


FIG. 2. 8 identical orbits centered at cube corners.

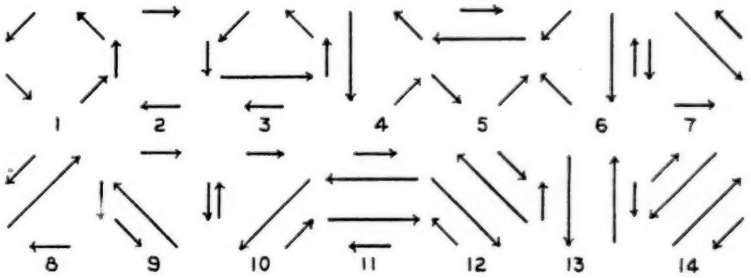


FIG. 3. Canonical bond eigenfunctions for 8 electrons, e.g., 2 is the bond eigenfunction *ab, cd, ef, gh.*

The three representations of the generating elements in this coordinate system are as follows:

$$\begin{array}{cccccccccccccc}
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & -1 & 0 & -1 & 0 \\
0 & 0 & -1 & -1 & 0 & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & -1 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1 & 1 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\
1 & 0 & 1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0
\end{array} \quad (12)$$

Three-fold

0	0	0	0	0	0	1	0	1	0	−1	0	−1	0
0	0	0	0	−1	−1	0	0	−2	0	0	0	0	1
0	0	0	0	0	0	0	0	−1	0	0	0	1	0
0	0	0	0	0	0	0	0	−1	0	1	0	0	0
0	0	1	0	0	−1	0	0	−1	0	1	0	0	0
0	0	0	1	−1	0	0	0	−1	0	0	0	1	0
0	0	0	0	0	0	0	0	1	0	0	0	0	0
0	0	0	0	1	0	0	0	1	1	0	0	−1	0
1	0	0	0	1	1	0	0	1	0	0	0	0	0
0	0	0	0	0	1	0	1	1	0	−1	0	0	0
0	0	0	0	0	1	0	0	1	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0
0	0	0	0	1	0	0	0	1	0	0	0	0	0
0	1	0	0	0	0	0	0	0	0	1	0	1	0

(13)

Four-fold

1	0	0	0	0	0	0	0	0	0	0	0	0	0
−2	1	−1	−1	−1	−1	0	0	0	0	0	0	0	0
−1	0	0	0	−1	0	0	0	0	0	0	0	0	0
−1	0	0	0	0	−1	0	0	0	0	0	0	0	0
−1	0	−1	0	0	0	0	0	0	0	0	0	0	0
−1	0	0	−1	0	0	0	0	0	0	0	0	0	0
1	0	0	0	1	1	0	0	1	0	0	0	0	0
1	0	0	1	1	0	0	0	0	1	0	0	0	0
1	0	1	1	0	0	1	0	0	0	0	0	0	0
1	0	1	0	0	1	0	1	0	0	0	0	0	0
1	0	1	0	1	0	0	0	0	0	1	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0
1	0	0	1	0	1	0	0	0	0	0	0	1	0
0	0	0	0	0	0	0	0	0	0	0	0	0	1

(14)

Inversion

By solving the Eqs. (8) we find the relations

$$a_1=2a_7-2a_{11},\quad a_3=a_4=a_5=a_6=-a_7+a_{11},\quad a_8=a_9=a_{10}=a_7,\quad a_{12}=a_{14}=a_2+2a_{11},\quad a_{13}=a_{11}, \tag{15}$$

so that the invariant sub-space is of dimensionality three and is spanned by the vectors

$$\begin{aligned}\Psi_1&=B_2+B_{12}+B_{14},\\ \Psi_2&=-2B_1+B_3+B_4+B_5+B_6-B_7-B_8-B_9-B_{10},\\ \Psi_3&=-2B_1+B_3+B_4+B_5+B_6+B_{11}+2B_{12}+B_{13}+2B_{14},\end{aligned} \tag{16}$$

which yields after suitable reduction the following secular equation

$$\begin{vmatrix} Q+2\alpha-8\beta-2\gamma-E & -(4/7)^{\frac{1}{2}}(\alpha+2\beta-3\gamma) & (20/7)^{\frac{1}{2}}(2\alpha-3\beta+\gamma) \\ -(4/7)^{\frac{1}{2}}(\alpha+2\beta-3\gamma) & Q-(46\alpha+32\beta-22\gamma)/7-E & (20/49)^{\frac{1}{2}}(4\alpha-3\beta-\gamma) \\ (20/7)^{\frac{1}{2}}(2\alpha-3\beta+\gamma) & (20/49)^{\frac{1}{2}}(4\alpha-3\beta-\gamma) & Q-(24\alpha+24\beta+8\gamma)/7-E \end{vmatrix}=0, \tag{17}$$

when Q is the coulombic integral for the system, α denotes the exchange integral between a and b, β that between a and c, and γ that between a and f.

That this eigenvalue is really the one for the lowest state may be seen if one computes the energy for eight Na atoms at the corners of a cube, and compares the value with that given by Taylor, Eyring and Sherman[13] which was obtained by a direct solution of the 14th order secular equation. For a cube edge of 3.15A the following values of Q, α, β and γ were used:

$$Q=94.4 \text{ kg cal.}; \qquad \alpha=12.69; \qquad \beta=6.88; \qquad \gamma=3.37.$$

Eq. (17) gives $E=69.9$ kg cal., which is to be compared with the value 68.1 kg cal. found by the other authors. This difference is within their computational error.

(3) Eight orbits possessing tetrahedral symmetry

The next case which we shall consider is that in which the arrangement of orbits possesses the symmetry group of a tetrahedron (T^d). This arrangement is met with, for example, in methane in which the four hydrogen atoms are situated at the four corners of a tetrahedron relative to the carbon atom at the center. A schematic diagram of the orbits is given in Fig. 4 in which the carbon orbits are designated by circles in circles and those of hydrogen atoms by dots in circles. The line connecting neighboring circles and dots is understood to be a prolongation of a body diagonal. The generating elements of the group T^d may be taken to be a three-fold rotation about the body diagonal through c and a vertical reflecting plane passing through df. With the canonical set of bond functions taken to be associated with Fig. 4 the representation of the threefold rotation is the same as (12), while that of the reflecting plane is

$$\begin{array}{cccccccccccccc}
1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & -1 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1
\end{array} \qquad (18)$$

Plane

The invariant subspace associated with this group is three dimensional and consists of the space spanned by the vectors

$$\psi_1=B_5, \qquad \psi_2=-3B_1+B_4+B_6-2B_9-2B_{10}+B_{11}+B_{12}+B_{14},$$
$$\psi_3=-B_1-2B_2+B_3-B_4-B_6+B_7+B_8+2B_{13},$$

and the secular determinant after suitable reduction is found to be[14]

[13] Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 68 (1933). Eyring and Kimball, J. Chem. Phys. **1**, 626 (1933).
[14] This equation has also been independently obtained by Eyring, Frost and Turkevich.

$$\begin{vmatrix} Q+4\alpha-3\beta-3\gamma-6\delta-E & 0 & (9/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) \\ 0 & Q-4\alpha-\beta-\gamma-2\delta-E & (5/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) \\ (9/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) & (5/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) & Q-4\beta-4\gamma-E \end{vmatrix}=0, \tag{19}$$

where α, β, γ and δ are the exchange integrals between ch, ah, bc and ac, respectively.

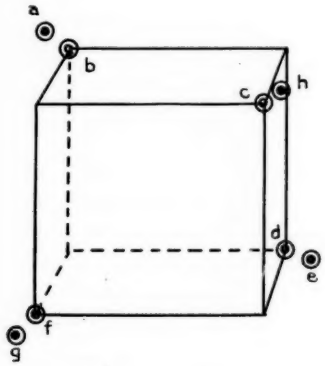


FIG. 4. 8 orbits possessing tetrahedral symmetry.

§4. VECTOR MODEL

As pointed out to us by Professor Van Vleck, our secular Eqs. (17) and (19) may be checked in various limiting cases with the aid of the vector model.[15] Use of the model is possible because the secular problem connected with the permutation degeneracy is formally equivalent, except for an additive constant, to that of cosine coupling between the spin vectors. This has been shown by Dirac, who demonstrated that the exchange effects between two states i and j are equivalent to a potential $-\frac{1}{2}J_{ij}[1+4\mathbf{s}_i\cdot\mathbf{s}_j]$, where J_{ij} is the exchange integral connecting i and j. The complete Hamiltonian function is therefore $Q-\frac{1}{2}\sum J_{ij}(1+4\mathbf{s}_i\cdot\mathbf{s}_j)$. The determination of the characteristic values of this function is in general quite complex, but if J_{ij} has the same value J for all pairs it may be taken outside the summation. Now consider the configuration of 8 orbits centered at cube corners, for the following cases:

(1) $\alpha=\beta=\gamma$. There are 8 electrons, 28 pairs.

$$\therefore\quad E=Q-\tfrac{1}{2}\sum_{1}^{28}\alpha-2\alpha\sum_{j>i}\mathbf{s}_i\cdot\mathbf{s}_j=Q-14\alpha-2\alpha\sum_{j>i}\mathbf{s}_i\cdot\mathbf{s}_j.$$

Since $\sum\mathbf{s}_i=0$, and $\mathbf{s}_i^2=\frac{3}{4}$, we have $\sum\mathbf{s}_i^2+2\sum\mathbf{s}_i\cdot\mathbf{s}_j=S(S+1)=0$, and $2\sum\mathbf{s}_i\cdot\mathbf{s}_j=-\frac{3}{4}\times8=-6$.

$$\therefore\quad E=Q-14\alpha+6\alpha=Q-8\alpha.$$

(2) $\alpha=\gamma=0$. Here the eight electron problem reduces to two identical four electron problems and the J can be taken outside the summation. From Fig. 2 it is clear that there are six β's,—i.e., six surface diagonals,—associated with each group of four electrons. Therefore,

$$E=Q-2[\tfrac{1}{2}\beta\sum(1+4\mathbf{s}_i\cdot\mathbf{s}_j)]=Q-2[3\beta+\beta\{S(S+1)-\tfrac{3}{4}\cdot4\}],$$

where S is the total spin of the four electrons, which may equal 2, 1 or 0 in this case.

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[15] See Dirac, Proc. Roy. Soc. **A123**, 714 (1929) or Dirac, *Quantum Mechanics*, Chapter XI, and Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Chapter XII. The vector model will also be discussed in forthcoming papers by Van Vleck and Serber.

$$\therefore \quad E=Q-2[3\beta+\beta(6-3)]=Q-12\beta \qquad \text{for } S=2,$$
$$E=Q-2[3\beta+\beta(2-3)]=Q-4\beta \qquad \text{for } S=1,$$
$$E=Q-2[3\beta+\beta(0-3)]=Q \qquad \text{for } S=0.$$

These are all roots of (17) in this case.

(3) $\alpha=\beta=0$. Referring to Fig. 2, there is only one body diagonal leaving any one corner, so that the problem obviously falls into four two-electron problems. The exchange energy in each of the four cases may be either $+\gamma$ or $-\gamma$, but since the total spin of the eight electrons is zero, E may equal either $Q\pm4\gamma$, Q, or $Q-2\gamma$. These are not all necessarily roots of (17) because this secular equation is associated with a symmetric wave function. Actually, the first three values of E are roots of (17).

Consider now the case of 8 orbits possessing tetrahedral symmetry, for the following cases:

(1) $\alpha=\beta=\gamma=\delta$. This will obviously give the same result as 1 above.

(2) $\beta=\gamma=\delta=0$. The secular problem is the same as 3 above, the characteristic values of each two-electron problem being either $+\alpha$ or $-\alpha$. E may equal $Q\pm4\alpha$, Q or $Q-2\alpha$. The first three values are all roots of (19) in this case.

(3) $\alpha=\delta$, β and $\gamma\neq0$. Here the Hamiltonian function becomes

$$Q-8\alpha-3\beta-3\delta-2\alpha\mathbf{S_C}\cdot\mathbf{S_{4H}}-2\beta\sum\mathbf{s}_i\mathbf{s}_j-2\gamma\sum\mathbf{s}_i\mathbf{s}_j$$
$$=Q-8\alpha-3\beta-3\delta-\alpha[\mathbf{S^2_{CH_4}}-\mathbf{S^2_C}-\mathbf{S^2_{4H}}]-\beta[\mathbf{S^2_{4H}}-\tfrac{3}{4}\cdot4]-\gamma[\mathbf{S^2_C}-\tfrac{3}{4}\cdot4],$$

where $\mathbf{S_C}=\mathbf{s}_1+\mathbf{s}_2+\mathbf{s}_3+\mathbf{s}_4$ denotes the spin of the carbon electrons and $\mathbf{S_{4H}}=\mathbf{s}_5+\mathbf{s}_6+\mathbf{s}_7+\mathbf{s}_8$ the collective spin of the four hydrogen electrons. In other words, the total spin of the carbons, and of the four hydrogen electrons, are good quantum numbers. The characteristic values of $\mathbf{S^2_{CH_4}}=S_{\mathbf{CH_4}}(S_{\mathbf{CH_4}}+1)$, $\mathbf{S^2_C}=S_{\mathbf{C}}(S_{\mathbf{C}}+1)$, $\mathbf{S^2_{4H}}=S_{\mathbf{4H}}(S_{\mathbf{4H}}+1)$, where $S_{\mathbf{CH_4}}$, $S_{\mathbf{C}}$ and $S_{\mathbf{4H}}$ are the total spins of CH_4, C and 4H's, respectively. The resultant spin of CH_4 is 0. Therefore $S_{\mathbf{C}}$ and $S_{\mathbf{4H}}$ must be equal and may of course be equal to 2, 1 or 0, corresponding to the values $Q+4\alpha-6(\beta+\gamma)$, $Q-4\alpha-2(\beta+\gamma)$ and $Q-8\alpha$ for the Hamiltonian, respectively.

In conclusion we wish to express our appreciation and thanks to Professor H. Eyring, A. Frost and J. Turkevich of Princeton University, and Professor J. H. Van Vleck of the University of Wisconsin, for helpful discussions in connection with the present work.

On the Theory of the Structure of CH_4 and Related Molecules: Part III

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(1) Use of Johnson's formulas for sp^3 levels in conjunction with existing experimental data makes it doubtful whether the ^5S state of the carbon atom is only 1.6 volts above the ground state, as often assumed in the literature. (2) A formula is derived for the energy of the "valence state" of the C atom, which is a linear combination of sp^3 levels wherein the spins are paired with those of attached atoms. This state is characteristic of tetravalent carbon compounds involving four electron pair bonds, and is shown to involve an increase of about 7 volts in the internal energy of the C atom over that in the ground state. (3) Because of this increment, the net or observed bonding energy is less than the gross or true inter-atomic bonding energy. The gross energy per bond is probably greater in CH_3 than in CH_4 although the reverse is true of the net. (4) A critical comparison is given of the Slater-Pauling theory of directed valence and the nondirectional Heitler-Rumer theory based on a ^5S state of the C atom. The former leads to much firmer bonds. (5) The assumption of electron pairing, made in Part II, is shown to be well warranted in CH_4, as it yields an energy value which is very nearly the same as the deepest root of Eyring and colleague's more exact cubic secular equation. (6) The energies of CH_4 and 4CH are compared in the light of theory.

1. Energy Levels of the Free Carbon Atom

In order for the carbon atom to exert its usual valence 4, it must be in the sp^3 configuration rather than in its normal state $s^2p^2\ ^3P$. In Part II,[1] all states (*viz.*, $^{1,3}P$, $^{1,3}D$, $^{3,5}S$) belonging to sp^3 were regarded as having the same energy, whereas we now wish to consider the influence of the L, S structure of this configuration, and in general to examine more carefully than previously the effect of the energy differences between s^2p^2 and sp^3.

First it is well to study the energy levels of the free carbon atom. The energies of the various states belonging to sp^3 have been calculated in terms of the Slater-Condon[2,3] F's, G's and I's by M. H. Johnson.[4] The results are given in Table I. We omit Johnson's spin-orbit terms, as they are very small for light atoms like carbon.

Table I.

State	Theoretical energy	Obs., C	Obs., N^+
$sp^3\ ^5S$	$W_0-3G_1-15F_2$		
$sp^3\ ^3S$	$W_0+G_1-15F_2$		19.2 volts
$sp^3\ ^3D$	$W_0-2G_1-6F_2$	7.9	10.4
$sp^3\ ^1D$	W_0-6F_2	9.7	
$sp^3\ ^3P$	W_0-2G_1	9.3	13.5
$sp^3\ ^1P$	W_0	9.7	

[1] Part I of the present series appeared in J. Chem. Phys. **1**, 177 (1933); Part II, ibid. **1**, 219 (1933). See Part I for references to the literature. We neglected to state there that the method of "molecular orbitals," which is the essence of the Hund-Mulliken procedure, was first introduced by J. E. Lennard-Jones, though only for diatomic molecules (Trans. Faraday Soc. **25**, 668 (1929)). The present article connects particularly with Section 5 of Part II, based on the Heitler-London method.

[2] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[3] E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

[4] M. H. Johnson, Jr., Phys. Rev. **39**, 209 (1932): These formulas for sp^3 may also be derived very simply by the Dirac vector model, as will be shown in a future paper by the writer in *Phys. Rev.* We have used this model to determine the additive constant in the energy, which was not specified in Johnson's paper since he took ^3D as the origin.

Here $$W_0 = I(2s) + 3I(2p) + 3F_0(2s; 2p) + 3F_0(2p; 2p) - W(s^2p^2\ {}^3P). \quad (1)$$

To avoid fractions, we use the Condon-Shortley[3] rather than Slater convention on the F's and $G's$, and $G_1(2s; 2p)$, $F_2(2p; 2p)$ are throughout abbreviated to G_1, F_2. The origin for the energy is always taken at the normal state $s^2p^2\ {}^3P$. The entries in the last two columns are the excitation energies of the spectroscopically known sp^3 states of C and N^+. Clearly the observed values are not compatible with the formulae, since different intervals yield discordant values of F_2 or G_1. For instance, ${}^1D - {}^3D$ of C demands $G_1 = 0.9$, while ${}^1P - {}^3P$ demands $G = 0.2$. This is not surprising, for the Slater relations seldom work well for light atoms. The observed energy of the ${}^3S$ term of N^+ however, is so unduly high as to suggest a misclassification, and hence possibly this term should be attributed to some other configuration than $2s2p^3$. Turner[5] indicates that such a misclassification is not unlikely.

The position of the ${}^5S$ state of C is of considerable interest in connection with the theory of valence. It has been suggested in the literature[5] that this state is 1.6 volts above the normal level. This estimate is based upon band spectra and cannot be considered reliable, as there is considerable doubt concerning the identification of the dissociation products, as well as in the extrapolation of the potential energy curves.

In our opinion the preceding table makes it probable, though not absolutely certain, that the ${}^5S$ state is not nearly as deep as 1.6 volts above normal. For instance according to the Johnson formulas it falls at 4.9 volts if we use the most favorable choice of the constants, *viz.*, the values

$$W_0 = 11.1, \qquad G_1 = 0.9, \qquad F_2 = 0.23 \text{ volts}, \quad (2)$$

which fit the observed ${}^3D$, ${}^3P$ and ${}^1D$ levels. The choice (2) does not give the correct position for the ${}^1P$ term, but conceivably this term might be abnormal because of a perturbation. If the constants are adjusted so as to fit ${}^1P$ at the expense of one of the three other known states, then ${}^5S$ is even higher than 4.9. Of course it is true that numerical values of the F's and G's do not mean a great deal as long as the Johnson formulas do not hold, but at the same time the fact remains that F_2 or G_1 would have to be of a different order of magnitude than required to fit other intervals if ${}^5S$ is really as deep as 1.6 volts. There appears to be no reason why ${}^5S$ should be unduly deep compared to the simple theoretical expectations. On the contrary, singlet and triplet states of the C atom belonging to other configurations than sp^3 are rather more abundant than the quintets and so perturbations by these other configurations will presumably tend to depress ${}^5S$ less than the other states of sp^3. If the ${}^5S$ state were as deep as 1.6, one would expect the ${}^4S$ state of C^+ to be abnormally low, since ${}^5S$ of C is based on a ${}^4S$ state of C^+, whereas ${}^{1,3}P$ and ${}^{1,3}D$ are based on ${}^2P$ and ${}^2D$. Actually ${}^4S$ of C^+ is only 1.14 volts[6] deeper than ${}^2D$, while ${}^2P$ is unknown.

An interesting calculation of the energy levels of the C atom has also been given by Beardsley.[7] He calculates the various exchange and Coulomb integrals, and so obtains explicit numerical formulas rather than expressions involving undetermined parameters I, F_2, G_1 such as we give. For our purposes, however, it appears better to use the formulas with parameters, as they bring out vividly the ratios between the various intervals, and do not require specialization of the wave functions except that they be of central character. The Beardsley paper naturally implicitly contains the Johnson formulas, for the ratios between the various intervals calculated by Beardsley are consistent with the simple theory. Beardsley's results correspond to the following choice of constants: $W_0 = 14.6$, $G_1 = 3.44$, $F_2 = 0.29$ volts. Such a choice locates ${}^5S$ at less than a volt above the ground level, and the "valence state" to be discussed in the next section at 4.0 volts. However, it gives a spread between the observed levels of sp^3 which is of a much greater order of magnitude than is observed experimentally in C, but which is of almost exactly the order observed in N^+. Of course

[5] W. Heitler and G. Herzberg, Zeits. f. Physik **53**, 52 (1929); L. A. Turner, Proc. Nat. Acad. **15**, 526 (1929).

[6] In their tables, Bacher and Goudsmit use different origins of energy for the doublets and quartets of C^+, but a common origin can immediately be secured by making use of the fact that absolute term values are known for both the triplets and singlets of C^{++}.

[7] N. F. Beardsley, Phys. Rev. **39**, 913 (1932).

it could be that the observed levels in C are abnormally close because of perturbations and that N^+ represents more nearly the usual state of affairs. We prefer, however, to blame the anomaly on ^3S of N^+, and to dismiss attempts to compute the intervals directly from the wave functions as unreliable because the latter are not known sufficiently well. The question, however, must be regarded as still an open one.

In view of all the above, we conclude that ^5S of C is probably 5 to 8 volts above the ground state, but 1.6 cannot be excluded with finality.

2. The Valence State of Carbon

The spread in energy among most of the states belonging to the configuration sp^3 is small compared to the energy difference between s^2p^2 and sp^3, or in other words the effect of the quantum numbers L, S on the energy is small compared to that of the individual l's. An exception is furnished by ^5S, especially if really at 1.6 volts, but this is only one state out of many. Hence it seemed plausible that in our calculations in Part II no great harm was done by ignoring the L-S structure. This point may now be made more quantitative and definite if one uses calculations by the Heitler-London-Pauling-Slater method as in Section 5 of Part II. It will turn out that the influence of the L-S structure on the directional valence is even smaller than one would conjecture.

In our calculations by the H-L-P-S procedure in II, the spins of the four electrons belonging to sp^3 were assumed paired with those of the four atoms attached by the carbon. Such a condition of the carbon atom we may conveniently call its valence state. It is not identical with any one of the six atomic states tabulated in Section 1, and is instead to be regarded as a linear combination of these. Its internal energy may be calculated, as follows in terms of the Slater F's and G's.

Let K_{ij} and C_{ij} (Slater's J) be respectively the exchange and Coulomb integrals connecting electrons i and j of the carbon atom. Do not confuse the intra-atomic exchange integral K_{ij} with the inter-atomic exchange integrals J_{ij} used in Part II. Since the C atoms all have their spins paired with those of electrons in attached atoms, the intra-atomic energy of the carbon atom is

$$W = I(3s) + 3I(3p) + \Sigma_{j>i}(C_{ij} - \tfrac{1}{2}K_{ij}) - W(s^2p^2\ ^3P) \tag{3}$$

when referred to the ground state. As emphasized in Part II, the coefficient $-\frac{1}{2}$ is characteristic of exchange effects between electrons paired otherwise than with each other. The C electrons have wave functions of the form

$$\psi_i = \alpha_i\psi(2s) + \beta_i\psi(2p\sigma_i) \tag{4}$$

where, as in Part II, $\psi(2p\sigma_i)$ means a $2p\sigma$ wave function when referred to the axis C-H_i. In virtue of the well-known vectorial transformation properties of the p wave functions, given for instance in (6) of II, one finds that

$$C_{ij} = \alpha_i^2\alpha_j^2C(2s;2s) + (\alpha_i^2\beta_j^2 + \beta_i^2\alpha_j^2)C(2s;2p) + 4\alpha_i\alpha_j\beta_i\beta_jK(2s;2p)\cos(i,j) + \beta_i^2\beta_j^2[C(2p\sigma;2p\sigma)\cos^2(i,j) + C(2p\sigma;2p\pi)\sin^2(i,j)], \tag{5}$$

$$K_{ij} = \alpha_i^2\alpha_j^2K(2s;2s) + \beta_i^2\beta_j^2[\cos^2(i,j)K(2p\sigma;2p\sigma) + \sin^2(i,j)K(2p\sigma;2p\pi)] + 2\alpha_i\alpha_j\beta_i\beta_j\cos(i,j)C(2s;2p) + [\alpha_i\beta_j\cos(i,j) + \alpha_j\beta_i]^2K(2s;2p) + \alpha_i^2\beta_j^2\sin^2(i,j)K(2s;2p). \tag{6}$$

Here $\cos(i,j)$ is the cosine of the angle between the axes C-H_i and C-H_j, and a common axis of quantization is to be understood in connection with all the Greek notation. Thus $C(2p\pi;2p\sigma)$ is the same as $J(211;210)$ in Slater's notation $J(nlm_l;n'l'm_l')$. The C's and K's on the right side of (5, 6) may immediately be expressed in terms of the F's and G's by means of Slater's tables (page 1312 of reference 2). We next sum over the various pairs of carbon electrons, as demanded by (3).

We can utilize the fact that the four wave functions (4) satisfy the relations

$$\alpha_i^2+\beta_i^2=1, \qquad \Sigma\alpha_i^2=1, \qquad \Sigma\beta_i^2=3, \qquad \alpha_i\alpha_j+\beta_i\beta_j\cos(i,j)=0,$$

because of the orthogonality and normalization to unity. These formulas materially simplify the final form of (3), which is found to be

$$W_v(\mathrm{C})=W_0+\tfrac{1}{4}(1-\mu)[F_0(2s;2s)-2F_0(2s;2p)+F_0(2p;2p)]-\tfrac{1}{2}(19+2\mu)F_2+\tfrac{1}{2}(-5+2\mu)G_1 \quad (7)$$

with W_0 as in (1) and $\mu=\alpha_1^4+\alpha_2^4+\alpha_3^4+\alpha_4^4$.

Since the hybridization ratios depend on the directions C-H_i, the expression μ is a function of the angles between the four valence directions of the C atom. It is rather remarkable that the only angular dependence is of the one type μ. The minimum value $\frac{1}{4}$ of μ is characteristic of the tetrahedral model, where all four electrons have the same hybridization ratio and hence $\alpha_1=\alpha_2=\alpha_3=\alpha_4=\frac{1}{2}$. The maximum value of μ is unity, and is achieved in a model without hybridization, i.e., a model where three of the valence directions are mutually orthogonal, and represent pure p bonds, while the fourth has an arbitrary direction, and corresponds to a pure s bond.

To form a numerical estimate of (7), we adopt for the various constants the values (2) together with

$$F_0(2s;2s)-2F_0(2s;2p)+F_0(2p;2p)=17.9-2\times16.1+14.8=0.5 \text{ volts.} \quad (8)$$

The result (8) is obtained theoretically from Beardsley's calculations,[8] as empirical methods are not feasible for this particular expression. The numerical value of (7) then ranges from 7.0 volts at $\mu=\frac{1}{4}$ to 7.3 volts at $\mu=1$. We thus conclude that:

(*a*) The effect of the *L-S* structure on the directional properties of valence is small, since the value of (7) varies but little with the choice of the valence directions as manifested in μ;

(*b*) The "valence" state of C has about 7 or 8 more volts of intra-atomic energy than the normal state. This is the energy required to make the C atom acquire a chemically active condition, but should not be confused with an "energy of activation" in the usual chemical sense, since the latter is lower because it includes allowance for the offsetting effect of the inter-atomic bonding energy.

Conclusion (*a*) would not be altered if different numerical values than (2), (8) were adopted, while the estimate 7 volts in (*b*) would be changed at most by a volt or two. This insensitivity is because F_2, G_1, and (8) are in any case small compared with (1), and the main term W_0 is known with at least moderate precision. We have already mentioned that smaller values of the F's and G's than (2) are obtained if we fit three other known states rather than ^1D, ^3D, ^3P as in (2). Hence our choice of the F's and G's tends, if anything, to overestimate the directional effect of the *L-S* structure and to underestimate somewhat the energy of the valence state. The individual terms in (8) are quite large, but the value of $F(2s;2p)$ is intermediate between $F(2s;2s)$ and $F(2p;2p)$ and somewhat less than their mean, so that the expression (8) is small and positive. These statements are true for almost any reasonable choice of Beardsley's parameters α, x, y and are not peculiar to his optimum selection $\alpha=5.7$, $x=1.3$, $y=0.6$ which we have used to obtain a numerical value in (8). Thus the order of magnitude of (8) seems fairly certain even though the particular value 1.5 may be considerably in error.

Analogous calculations on the effect of the *L-S* structure could also be made for other compounds, where the valence is 2 or 3 rather than 4, and where in consequence the state of the central atom is intermediate between s^2p^2 and sp^3. These computations, however, do not seem worth while, as in Section 6 of Part II our theory included allowance for the individual l's on the energy, and it seems reasonably clear from the above that the *L-S* refinement will be unimportant at the present state of accuracy of valence theories.

[8] The expressions αK, $\alpha(O+\frac{3}{5}P)$, αP, αQ, on page 918 of Beardsley's paper are respectively the same as $F_0(2s;2p)$, $F_0(2p;2p)$, $3F_2$, $F_0(2s;2s)$ in our notation.

3. Relative Energy of CH_3 and CH_4

Mulliken[9] emphasizes the fact that the apparent energy per bond has a larger value, 4.0 volts, in CH_4 than in CH_3, where he estimates the value to be 3.6 volts or less. In our opinion this is not because the true inter-atomic bond energy is greater in CH_4 than in CH_3, but simply because the C atom must be excited to the "valence state" before it can form either a trivalent or quadrivalent compound. Once it has been thus excited at the expense of unfavorable intra-atomic energy, it is clearly in the best interests of the atom to form as many bonds as possible. We must distinguish between net and gross energy per bond, the former being that observed experimentally, and the latter the true inter-atomic bond energy obtained by increasing the experimental value by the energy of excitation of the valence state prorated to the different bonds. The values quoted by Mulliken are net. If we assume that this excitation energy is 7.1 volts, the corresponding gross values are 5.8 volts for CH_4 and 6.1 volts, or less, for CH_3.

Theoretically, the gross energy per bond should be somewhat higher in CH_3 than in CH_4 for two reasons. In the first place the repulsive energy between the H atoms should be less in CH_3 than in CH_4, due to a removal of an H atom. In the following section we shall estimate the H-H repulsive energy to be 2.5 volts in CH_4. The corresponding value in CH_3 is 1.2, as there are here 3 rather than 6 repulsive H pairs. This is on the assumption that the tetrahedral angles are preserved in CH_3. With a plane model, the repulsive energy is further reduced from 1.2 to 1.0 volts. In the second place, quite irrespective of H-H repulsions, the true C-H valence energy per bond should, if anything, theoretically be somewhat greater in CH_3 than in CH_4. With the Heitler-London-Pauling-Slater method, one can see this most readily by noting that the energy per bond is identical in CH_3 and CH_4 if the tetrahedral angles are preserved in CH_4 (*viz.*, when $\theta=109.5°$, the expression (37) of Part II is exactly 3/4 as large when $\mathfrak{N}=0$ as when $\mathfrak{N}=N$). Now in Part II we saw that, even without H-H repulsions, the tetrahedral angles were not the best, and that a somewhat flatter model gave lower total energy for the CH_3 molecule, or in other words higher bonding energy. Hence when the most favorable angles are used, the energy per bond will be increased over the tetrahedral or CH_4 value. The increase, however, is not large, as the variation of (37) of II with θ is not great. In fact the difference in the value of (37) for the tetrahedral and plane models of CH_3 is

$$W_t - W_p = 0.375(N_{ss} - N_{\sigma\sigma}) + 0.345N_{\sigma s}.$$

We shall see in the next section that $N_{ss}-N_{\sigma\sigma}$ and $N_{\sigma s}$ are probably not more than a volt or so in magnitude, and possibly of opposite sign. So the decrease in energy occasioned by departures from the tetrahedral angles probably does not amount to more than a fraction of a volt. With any given values of $N_{\sigma\sigma}$, N_{ss}, $N_{\sigma s}$ the best value of the angles could be determined by means of (44) of Part II, but the N's are not known with sufficient precision to make this repaying. With the Hund-Lennard-Jones-Mulliken method, it is not possible to reach as definite conclusions on the relative magnitudes of the energies per bond in CH_3 and CH_4. With forms (i) and (ii) of this method given on page 237 of Part II, the energy per bond appears to be greater in CH_3 than in CH_4, but with (iii) the reverse is apparently sometimes true.

Instead of comparing the energies per bond in CH_3 and CH_4, it is often convenient to examine instead the energy of the reaction $CH_4=CH_3+H$, since Mulliken's estimates of the energy per bond in CH_3 are simply deduced from an assumed energy for this reaction along with a known heat of formation of CH_4 from C+4H. His net value 3.6 volts per bond in CH_3 is under the assumption that removal of an H atom from CH_4 requires 5 volts. Mulliken concludes from ionization potential data, etc., that the energy connected with this removal is between 5 and 7 volts, and is probably much nearer 5 than 7. Any increase above 5 is reflected in a decrease of the net CH_3 value below 3.6. We may attempt an estimate of the heat of the reaction $CH_4=CH_3+H$ from our theory. The gross energy per bond in CH_4 is increased from 5.8 to 6.4 volts when we correct for the H-H repulsions so as to have the pure C-H energy rather than the resultant of C-H and H-H actions. With the

[9] R. S. Mulliken, J. Chem. Phys. 1, 500 (1933).

H-L-P-S method one should expect the energy of the process $CH_4 = CH_3 + H$ to be about $1\frac{1}{2}$ to 2 volts less than the corrected gross energy per bond in CH_4, the difference arising because of the two effects noted in the preceding paragraph. Thus by an entirely different method we roughly confirm Mulliken's estimate that this process requires about 5 volts.

4. Comparison with the Heitler-Rumer Theory

Besides the Hund-Lennard-Jones-Mulliken and Slater-Pauling theories which we have discussed in detail in Parts I and II, still another and somewhat earlier theory of valence in carbon and nitrogen compounds has been given by Heitler and Rumer.[10] The H-R theory, like the S-P one, is based on the Heitler-London method, but, unlike S-P, does not introduce electron pairing. Instead the valence electrons of the central atom have their maximum possible resultant spin, so that in carbon and in nitrogen compounds the C and N atoms are respectively in ^5S and ^4S states. In the S-P theory, on the other hand, the spin of the central atom is not a good quantum number, and the spin of each C or N electron is compounded with the spin of an electron of an attached atom to give zero resultant spin for the two, which thus constitute an electron pair. In the S-P form all the private properties of the central atom are sacrificed in order to give "maximum overlapping" between the two wave functions involved in an electron pair. As a result the L and S of the central atom cease to be good quantum numbers, while the hybridization spoils even the l's of the individual electrons. In the H-R theory, L, S, and the l's are all good quantum number, but at the expense of having less overlapping. Whether the S-P or H-L method is the better approximation depends upon whether the total energy of the chemical bonds is large or small compared to the separation between the various terms belonging to the electron configuration of the central atom (configuration sp^3 in C; s^2p^3 in N), or, in other words, upon whether it is more important to diagonalize the intra-atomic or inter-atomic part of the Hamiltonian function. We shall examine this question somewhat quantitatively in the next few paragraphs, and we shall see that usually the S-P approximation is the better one.

Before doing this we must caution that when we speak of the S-P and H-R theories, we always mean them in their most restricted forms, as this usage furnishes a terminology for different simple methods of approximation. Extended forms of the theories cease to be so sharply delineated. The original H-R paper did, indeed, treat all valence orbits of the central atom as identical and as effectively s-states, thus abnegating all directional valence effects, but Heitler and Rumer doubtless did not mean to imply that directional properties should not ultimately be considered in a more refined theory. Similarly, the S-P wave functions lend themselves particularly aptly to electron pairing, but both Slater and Pauling have abandoned the restriction to unique pairs or bond structures in certain of their calculations, *viz.*, those of Slater[11] on the water molecule and especially those of Pauling on "resonance" in complicated organic molecules.[12]

Under the assumption of electron pairing, the expression for the energy of formation of the CH_4 molecule is

$$W(CH_4) - W(C+4H) = W_V(C) + 0.5N_{ss} - 2.5N_{s\sigma} + 4N_{\pi\pi} - 5.196N_{\sigma s} + W_{\text{ion}}(CH_4) + W_{\text{coul.}}(CH_4) + 6\times(-0.35)M(H_2) \quad (9)$$

if one utilizes the Slater-Pauling hybridized wave functions. Here, as in Part II, the N's have the significance

$$N_{kl} = -\int\int\int\int\int\int \psi_H(1)\psi_k(2)\mathbf{H}\psi_l(1)\psi_H(2)dv_1dv_2 \quad (k, l = 2s, 2p\sigma, \text{ or } 2p\pi \text{ of C}), \quad (10)$$

[10] W. Heitler and G. Rumer, Zeits. f. Physik **68**, 12 (1931).

[11] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[12] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933); L. Pauling and I. Sherman, ibid. **1**, 679 (1933).

and, except for N_{ss}, are the negative of ordinary exchange integrals. The portion of (9) involving the N's, i.e., the C-H exchange contributions, was derived in Eq. (37) or (38) of Part II, when the angles in (37) or (38) are specialized to tetrahedral values. As compared with Part II, we now use a more complete expression for the energy of formation, as we now include the internal energy of excitation $W_V(\mathrm{C})$ of the valence state of the C atom, given by (7) with $\mu=\frac{1}{4}$, the Coulomb energy between the C and H atoms, an ionic term, and the energy due to forces between the hydrogen atoms, which is the last term in (9). The Coulomb portion was not explicitly included in (37) or (38) of Part II partly because it is somewhat subordinate to exchange terms, and especially because we were interested in II primarily in the dependence of the energy on the arrangement of the attached atoms. One can easily show that in compounds of the structure $CWXYZ$, wherein the C atom attaches any four univalent atoms W, X, Y, Z, and in which the C atom is in the configuration sp^3 either with or without hybridization, the Coulomb energy connecting the C atom with the attached atoms is independent of how these atoms are arranged in space as long as their distances from the C atom are not varied. Hence the considerations in Section 5 of Part II are not affected. In the present discussion the Coulomb energy must be included since we are considering absolute energy of formation rather than just directional dependence.

The ionic term is included in order to allow for the fact that in CH_4 the C atom doubtless acquires some negative charge at the expense of the four hydrogens. This term, again, is important for absolute bonding energies, but probably does not vary greatly with the orientation of the valence axes, so that it was sufficiently allowable to omit the ionic effect in Part II.

In the last, or H-H term of (9), the symbol $M(H_2)$ denotes a Morse function for the normal state of the H_2 molecule. Following Eyring and Polanyi,[13] we have assumed that H-H bonding can be represented by a Morse function, and that this bonding is ten percent Coulomb and ninety percent exchange. The factor $-0.35=0.1-\frac{1}{2}\times 0.9$ owes its origin to the fact that the exchange coefficient between members of different pairs is $-\frac{1}{2}$. The factor 6 is, of course, simply because there are six H-H pairs in all. According to the Raman data of Dickinson, Dillon and Rasetti on the moment of inertia of CH_4, the C-H and H-H separations are respectively 1.08 and 1.77 Angstroms. With $r=1.77\times 10^{-8}$, one finds $M(H_2)=-1.18$ volts.

With the Heitler-Rumer theory, where the carbon atom is in a ^5S state, the expression corresponding to (9) is

$$W(CH_4)-W(C+4H)=W(^5S)-N_{ss}-N_{\sigma\sigma}-2N_{\pi\pi}+W_{\mathrm{ion}}(CH_4)+W_{\mathrm{coul.}}(CH_4)+6\times(-0.8)M(H_2). \tag{11}$$

Here $W(^5S)$ is the excess of energy of $sp^3\ ^5S$ over the ground state $s^2p^2\ ^3P$ of C. The H-H term now has a factor $-0.8=-1\times 0.9+0.1$ rather than -0.35 because the spins of all the H atoms must be mutually parallel in order to be able to neutralize the spin $S=2$ of the C atom, and this requires that the exchange coefficient for each H-H pair be -1. Heitler and Rumer give $+4(\mathrm{CH})$ for the C-H exchange term, where (CH) denotes the C-H exchange integral. However, they regard all four two-quantum orbits of the C atom as identical. When we allow for difference in sign convention, and distinguish between the various types ($2s$, $2p\sigma$, $2p\pi$) of C orbits, their $+4(\mathrm{CH})$ becomes replaced by $-(N_{\sigma\sigma}+N_{ss}+2N_{\pi\pi})$, in our notation. This is fairly obvious from the fact that the ^5S state of C has the structure $2s2p\sigma 2p\pi^2$ when referred to *any* set of Cartesian axes x, y, z.[14] Another derivation of the N terms will also be given in Section 5.

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[13] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **12**, 279 (1931); H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931). Dr. A. Sherman informs the writer that it is better to take the exchange part as 86 rather than 90 percent of the Morse function, at least in calculations of activation energies. This modification is too small to be of consequence for our work, and so we use the round value 90.

[14] For a quintet state involving four electrons, the Pauli principle allows only one electron to each orbital state. There are two kinds of $2p\pi$ states, *viz.*, the left- and right-handed varieties, or orthogonal linear combinations thereof.

The expressions $N_{\sigma\sigma}$, N_{ss}, $N_{\sigma s}$ are all positive, while $N_{\pi\pi}$ and $M(H_2)$ are negative. Hence all the N terms except that involving N_{ss} have lower values in (9) than in (11), meaning that the C-H exchange effects tend to make the S-P structure more stable than the H-R one. The forces between the attached H atoms also favor S-P, as can be seen by comparing the last terms of (9) and (11). The first or internal carbon term is deeper in (11) than in (9), but not enough so to offset the influence of the other terms. To examine this point more quantitatively, let us assume that the first terms of (9) and (11) can be calculated respectively by (7) and Johnson's formula with the constants (2), and that the constants involved in the other terms of (9, 11) have the following magnitudes

$$N_{\sigma\sigma}=+2.3, \qquad N_{ss}=+2.0, \qquad N_{\pi\pi}=-0.6, \qquad N_{\sigma s}=+1.0, \qquad M(H_2)=-1.18 \text{ volts.} \quad (12)$$

This choice for $N_{\sigma\sigma}$ and $N_{\pi\pi}$ is suggested by an analysis of C-H potential energy curves to be published by J. R. Stehn and the writer, as well as by Coolidge's calculations on the H_2O molecule.[15] The basis for the choice of $N_{\sigma s}$ will be given below. Coolidge's work indicates a somewhat larger value of N_{ss} than $N_{\sigma\sigma}$, but this does not allow for the fact that the $2s$ wave functions are screened less from the C nucleus than the $2p$, so that they are drawn in more and tend to overlap the hydrogen atoms less. Hence we take for N_{ss} the round value two volts.

With the choice of constants discussed in the preceding paragraph, the value of (9) is 10.2 volts lower than that of (11). The corresponding value of $W(^5S)$ is 4.9 volts (cf. Section 1). However, even if instead of using this theoretical estimate based on Johnson's formula we take $W(^5S)=1.6$ volts, the doubtful spectroscopic value sometimes quoted, the expression (9) is still 6.9 volts below (11).

It is not surprising that the S-P approximation gives a firmer binding than the H-R one, for the latter lacks the favorable overlapping which is the essence of directional valence, and which is reflected particularly in the low value of the $N_{\sigma\sigma}$, $N_{\sigma s}$ terms in (9). The importance of directional valence is shown particularly clearly by the actual pyramidal structure of the ammonia molecule. If one makes a H-R calculation based on a ^4S state of the nitrogen molecule, one predicts a plane model for the molecule, as the only directional effects are the H-H repulsions. This difficulty is avoided when one makes a calculation based on electron pairing and directed valence, as in Part II.

5. Comparison with More Accurate Solution, not Requiring Electron Pairing

Eyring, Frost and Turkevich[16] have ingeniously demonstrated that the secular problem connected with the permutation degeneracy in the Slater-Pauling sp^3 model of methane can be solved without the necessity of assuming electron pairing. This is feasible, as they show, because the tetrahedral symmetry permits extensive factorization of the secular equation, which otherwise would be of degree 14 for the states of zero spin. The factor in which we are interested corresponds to the Bethe representation Γ_1, and leads to an algebraic equation for W of degree 3. This cubic is given in convenient form by F. Seitz and A. Sherman in Eq. (19) of their paper,[17] which immediately precedes our own in the present issue, and so need not be repeated here. Their constants α, β, γ, δ, Q have the following significance in terms of the more rudimentary and fundamental constants which we have used

$$-4\alpha=N_{ss}+3N_{\sigma\sigma}+2\sqrt{3}N_{\sigma s}, \qquad \beta=0.9M(H_2), \quad (13)$$

$$16\gamma=F_0(2s;2s)-2F_0(2s;2p)+F_0(2p;2p)+28F_2+4G_1, \quad (14)$$

$$-12\delta=3N_{ss}+N_{\sigma\sigma}+8N_{\pi\pi}-2\sqrt{3}N_{\sigma s}, \quad (15)$$

[15] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

[16] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).

[17] F. Seitz and A. Sherman, J. Chem. Phys. **1**, 11 (1934). The appropriate cubic secular determinant is given in this paper in a form in which W appears only down the principal diagonal and which hence facilitates the application of perturbation theory. In reference 16, a less convenient, non-orthogonal form is given. The writer is indebted to the various authors mentioned in notes 16 and 17 for the opportunity of seeing their manuscripts in advance of publication.

$$Q=\tfrac{3}{8}[F_0(2s;2s)+6F_0(2s;2p)+9F_0(2p;2p)-12F_2-4G_1]+I(2s)+3I(2p)$$
$$-W(s^2p^2\,{}^3P)+W_{\text{ion}}(CH_4)+W_{\text{coul.}}(CH_4)+0.6M(H_2). \quad (16)$$

Formula (14) is an immediate consequence of (6) specialized to tetrahedral angles. The term Q consists of six times the expression (5), so specialized, plus $I(2s)+3I(2p)-W(^3P)$ and the proper inter-atomic terms, thus yielding (16). The formula for β is merely a statement of our apportionment of the Morse function for H_2 between exchange and Coulomb effects. The values of α and δ follow from the rotational transformation properties of sp^3 wave functions (cf. page 232 and Eq. (6) of Part II.)

If α is negative and large in absolute magnitude compared to β, γ, δ the deepest root of the cubic equation mentioned above is approximately

$$W=Q+4\alpha-3\beta-3\gamma-6\delta-[9(\beta-2\delta+\gamma)^2/2(-4\alpha-\beta-\gamma+6\delta)]. \quad (17)$$

Here the terms outside the brackets embody the result of first order perturbation theory (retention of only diagonal elements in Eq. (19) of Seitz and Sherman) and give exactly the same expression as that (9) characteristic of electron pairing. The bracketed part of (17) is yielded by second order perturbation theory, applied to the cubic under the assumption that α is much larger in absolute magnitude than the other constants. Use of (2), (8) and (12) in (13–16) gives

$$\alpha=-3.09, \quad \beta=-1.06, \quad \gamma=+0.67,$$
$$\delta=-0.01 \text{ volt}. \quad (18)$$

With these numerical values, the bracketed portion of (17) amounts to less than a tenth of a volt. Thus electron pairing is an exceedingly good approximation for a H-L-P-S calculation in methane. The particular numerical estimate of an error less than 0.1 volt which we have given is perhaps a little optimistic, since the particular choice (12) happens to make the constant δ, which appears prominently off the diagonal in the Seitz-Sherman Eq. (19), almost vanish. However, one finds that one can vary any of the constants (except $N_{\pi\pi}$, which is fortunately probably the best known) a volt or so from the values (12) and still the bracketed part of (17) usually remains less than a volt. Instead of using second order perturbation theory to gauge the error involved in electron pairing, one could, of course, solve the cubic numerically, and compare with (9), but this is clearly unnecessary.

In the previous paragraph we examined the absolute error involved in electron pairing. It is also instructive to study the relative error in the sense of how large the bracketed term of (17) is compared to the separation of the roots of the cubic. One finds that with (18) and either first or second order perturbation theory, the other two roots are respectively 12 and 24 volts above (17), which alone represents favorable pairing. Thus the relative error is also small. The other roots are clearly not adapted to chemical bonding.

It is clearly to be understood that although electron pairing is a good approximation for solving the cubic, this does not at all imply that the underlying Heitler-London procedure is satisfactory. Also electron pairing is not always feasible for other problems than methane. For instance, there is no natural scheme of pairing for Seitz and Sherman's other cubic Eq. (17) which applies to eight atoms at the corners of a cube.

If γ is positive and large in magnitude compared with α, β and δ, the deepest root of the cubic Eq. (19) of Seitz and Sherman is

$$Q-6\gamma+3\delta+\alpha-6\beta.$$

With the aid of (13–16) and Johnson's formula for $W(^5S)$ one finds that this is the same expression as (11). We thus have an additional proof of (11) in the Heitler-Rumer theory. This does not, however, mean that use of (11) is legitimate, for (18) shows that γ is not large in magnitude compared to the other constants. Consequently the spin of the central atom is not a good quantum number, and we again conclude that the H-R assumption of a central ^5S state is not warranted. In short, Eqs. (9) and (11) are

asymptotic solutions of the cubic under different limiting conditions, which actually are nearly fulfilled only in the case of (9).

When inter-atomic terms are omitted, one of the roots of the cubic reduces, as we have seen, to the energy $W(^5S)$ of the quintet state of the carbon atom. We must not expect the other roots to reduce similarly to other of the Johnson levels given in Section 1, for in order to obtain the cubic, it was necessary for Eyring and his school to assume hybridized sp^3 wave functions. Now the states of the free C atom cannot be represented by hybridized, rather than pure s and pure p, wave functions except in the special case of quintets. With the latter, the orbital portion of the wave function is antisymmetric, and hence when it is written out explicitly in the form

$$\Sigma_{ijkl} a_{ijkl} \psi_i(x_1)\psi_j(x_2)\psi_k(x_3)\psi_l(x_4)$$

where i, j, k, l can be chosen from $2s$, $2p\sigma_x$, $2p\sigma_y$, $2p\sigma_z$, the coefficients will vanish unless i, j, k, l all refer to different orbital states. The hybridization of the central atom is thus only "apparent" when the spin of the central atom has its maximum value. Except when the Heitler-Rumer hypotheses are literally valid, there is always a certain amount of error committed in assuming that the complete molecular wave function can be constructed out of sp^3 wave functions. Hence even the cubic given by Eyring, Frost and Turkevich, or by Seitz and Sherman, does not represent a complete first order Heitler-London calculation. (As here used, the term "first order" means neglect of polarization, and has nothing to do with the orders involved in the two parts of Eq. (17).) In other words, the L-S structure of the carbon atom is not rigorously treated by the inclusion of the γ terms in their cubic determinant. Section 2 shows that this structure is not of dominating importance, and so the resultant error is not serious, probably of about the same size as the terms of order γ^2 in (17).

6. Relative Energy of CH_4 and 4CH

It is interesting to compare the expression (9), based on electron pairing, with the observed energy of formation of CH_4 from C and H atoms. Not much in the way of numerical agreement is to be expected, since the N constants are not known accurately, and especially since (9) neglects triple and higher permutations and the lack of orthogonality of the various H and C wave functions. Because but little is known about the magnitudes of $W_{\text{coul.}}$ and especially W_{ion}, it is instructive to compare the energy of CH_4 with that of 4CH rather than of C+4H. These magnitudes then do not enter if one assumes as a rough approximation that the Coulomb and ionic terms are four times as large for CH_4 as for the diatomic molecule CH. One can show[18] that under the assumption of electron pairing, the energy of CH is

$$W(\text{CH}) - W(\text{C}+\text{H}) = k - N_{\sigma\sigma} + N_{ss} + \tfrac{1}{2}N_{\pi\pi} + W_{\text{ion}}(\text{CH}) + W_{\text{coul.}}(\text{CH}), \quad (19)$$

where $k = 0.315$ volt is one-fourth the separation of the ^3P and ^1D terms of the C configuration s^2p^2. Hence if as usual we take the ground state of C as the origin of energy

$$W(\text{CH}_4) - 4W(\text{CH}) = W_V(\text{C}) - 4k - (7/2)N_{ss} + (3/2)N_{\sigma\sigma} + 2N_{\pi\pi} - 5.196N_{\sigma s} - 2.10M(\text{H}_2). \quad (20)$$

The actual bonding energy of CH_4 is 17.3 volts according to thermochemical data,[19] while that of CH is 4.0 according to a rather uncertain

[18] Eq. (19) is proved by the same methods as given in Section 5 of Part II or in fine print in J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933). Concerning the need of the k term see note 13 of the latter reference.

[19] This numerical value is taken from L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933). Mulliken bases his calculations on a lower value 15.8 volts. To facilitate comparison with Mulliken's article, we have utilized 15.8 rather than 17.3 volts as the heat of formation of CH_4 in all our estimates of the relative energies of CH_3 and CH_4 in Section 3. Use of 17.3 instead of 15.8 would not affect our conclusions in Section 3 that the gross energy per bond is greater in CH_3 than CH_4, and that our theory leads to an energy for the reaction $CH_4 = CH_3 + H$ of approximately the proper magnitude 5 volts. This is all, of course, provided the promotional energy to the valence state of carbon is 7 volts or more. If it is only about 4 volts, as is the case provided there is really a ^5S state only 1.5 volts above normal, or provided we accept Beardsley's numerical estimates of the F's and G's, the gross energies per bond are nearly equal in CH_3 and CH_4. In this case $W_V(C) \sim 4$ volts, Eq. (20) demands $N_{\sigma s} = 0.4$ rather than 1 volt.

estimate by Mulliken[20] from band spectra. The empirical value of the left side of (20) is thus roughly -1.3 volts. This value is also obtained for the right side if one assumes that the various constants have the values (2), (6) and (12). These values were all obtained from semi-empirical, semi-theoretical considerations except that the value of $N_{\sigma s}$ is then regarded as unknown and is arbitrarily adjusted to give (20) the observed value. One may also form a rough estimate of $N_{\sigma s}$ from theoretical calculations involving the evaluation of inter-atomic integrals. Such calculations of Ireland[21] on BeH suggest that $N_{\sigma s}$ should be somewhat larger than $N_{\sigma\sigma}$ or N_{ss}, although exact comparison is difficult because the N's are not uniquely defined unless the various wave functions are orthogonal, which actually they are not. Thus one would guess that $N_{\sigma s}$ is at least as large as 2 volts. Some reasons why our estimate 1 volt by means of (20) may be too low are the following: (a) N_{ss}, which gives an important term in (20) may be less than 2 volts, (b) the values of W_V(C) may be a volt or so more than 7.0 volts for reasons explained in Section 2, (c) we have not considered the corrections for the "zero point" or residual half-quantum vibrational energy, (d) the Coulomb terms of CH_4 may not be 4 times as great as those of CH. Use of a factor 4 seems warranted in the ionic part, but the Coulomb energy of CH_4 is only 8/3 that of CH if one assumes for instance, that the Coulomb integrals involving $2p\sigma$ and $2s$ are equal, while those for $2p\pi$ are negligible. The residual vibrational terms will cancel to a large extent in a comparison of CH_4 with 4CH, but not entirely so, since CH_4 has more than four times as many vibrational degrees of freedom as CH. It is doubtful, however, whether all these effects (a)–(d) alter the right side of (20) by more than a few volts, so that according to (20) it is hard to see how $N_{\sigma s}$ could in any case be more than 1.5 or possibly 2 volts. This still seems somewhat small, but one yet has the errors due to non-orthogonality and higher permutations, and even when these errors are eliminated, Heitler-London calculations seldom agree quantitatively with experiment. In any case one qualitative conclusion is clear. It is purely accidental that the bonding energy in CH_4 is almost exactly four times that in CH. The exchange and hybridization effects are such that the *gross* energy per CH bond is greater in CH_4 than in CH. However, the CH_4 molecule involves excitation of the C atom to the sp^3 state, and H-H repulsive energy, both of which do not enter in CH, and this is why the *net* energies per bond can fortuitously be nearly equal in CH_4 and CH.

Before closing, we must by all means mention that a calculation of the heat of formation of CH_4 has also been made by H. J. Woods.[22] He endeavors to compute the absolute bonding energy, or in other words compares CH_4 with C+4H rather than 4CH. Like us, he assumes electron pairing, although he does not list the contribution of the various elementary integrals in quite the explicit form (9). He does not include any ionic term or examine at all closely the internal energy of the C atom, and we are inclined to believe that the good agreement which he obtains with experiment is in part accidental.[23] In many respects Woods's calculations represent considerably more refinement than ours. In particular, he considers the corrections arising from want of orthogonality, and to a certain extent the higher permutations. Also he proceeds to his answer by really evaluating the inter-atomic integrals such as (10), etc., a task which we have eschewed throughout the present series. Since the numerical success of the Heitler-London method is now known to be rather limited, we have concentrated primarily on the study of the semi-quantitative results, notably the directional effects, which can be deduced from the general structure of the formulae without the need of too accurate numerical knowledge of exchange integrals and the like.

[20] R. S. Mulliken, Rev. Mod. Phys. **4**, 80 (1932).
[21] C. Ireland, Phys. Rev. **43**, 329 (1933).
[22] H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).
[23] If the promotional energy to the valence state of C is 7 volts, the gross energy per bond in CH_4 is 6 volts, rather than 5 as stated by Woods.

Potassium Superoxide and the Three-Electron Bond*

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The highest oxide of potassium is shown to be paramagnetic, with a susceptibility corresponding to the formula KO_2, the crystals being supposed to contain O_2 ions in a $^2\Pi$ state. The electronic structure $:\dot{\ddot{O}}:\dot{\ddot{O}}:^-$ is proposed for the superoxide ion. It is suggested that the substance be called potassium superoxide rather than tetroxide.

IN stating his rule that the number of valence electrons present in a molecule is a multiple of two, Lewis[1] pointed out that a number of substances, namely, NO, NO_2, ClO_2, the so-called free radicals of Gomberg, and the divalent nitrogen compounds of Wieland, are exceptions to the rule, inasmuch as the molecules of these substances contain an odd number of valence electrons. He termed such molecules "odd molecules." He noted that they are paramagnetic, and that most of them absorb very strongly in the visible region of the spectrum, that is, are highly colored.

In order to account for the stability of NO, NO_2, etc., Pauling,[2] in a discussion of the nature of the chemical bond, argued that no single electronic structure with the odd electron on a given atom can satisfactorily represent the structure of the molecule. He then introduced the idea that the molecule resonates among several electronic structures, the accompanying extra resonance energy tending to stabilize the molecule. Thus in the case of NO he postulated two structures which were represented by $:\dot{N}::\dot{O}:$ and $:\dot{N}::\ddot{O}:$. He found these two structures to have nearly the same energy, in which case resonance between them would lead to a more stable combined structure having a double bond and a three-electron bond, which he represented by $:N\dddot{:}O:$. A similar treatment was accorded NO_2 which he represented by ($:\dot{\ddot{O}}\dddot{:}N::\dot{\ddot{O}}:$, $:\dot{\ddot{O}}::N\dddot{:}\dot{\ddot{O}}:$), the double bond changing places regularly with the single and the three-electron bond. He also discussed the normal state ($^3\Sigma$) of the oxygen molecule, containing one electron-pair bond and two three-electron bonds, corresponding to the structure $:\dot{O}\dddot{:}\dot{O}:$.

Recently Brockway[3] has examined ClO_2 by electron diffraction methods, and has found that the observed chlorine-oxygen distance in this compound is compatible with the presence of a three-electron bond and an electron-pair bond between the chlorine and one oxygen, and an electron-pair bond between the chlorine and the other oxygen. He represented this electronic structure by ($:\dot{\ddot{O}}\dddot{:}\dot{\ddot{C}}l:\ddot{O}:$, $:\ddot{O}:\dot{\ddot{C}}l\dddot{:}\dot{\ddot{O}}:$).

The highest oxide of potassium is commonly known as the tetroxide, K_2O_4. A reasonable electronic structure for the $O_4^=$ ion is $:\ddot{O}:\ddot{O}:\ddot{O}:\ddot{O}:^=$. Such a structure corresponds to a colorless and diamagnetic substance. If, however, the formula of the substance were KO_2, it would contain O_2^- ions, for which we could write the structures $:\dot{\ddot{O}}:\ddot{O}:^-$ and $:\ddot{O}:\dot{\ddot{O}}:^-$. These two have the same energy; resonance between them would give a $^2\Pi$ state, $:\dot{\ddot{O}}\dddot{:}\dot{\ddot{O}}:^-$, with a three-electron bond between the oxygen atoms. An ion such as this, containing an odd number of electrons, would cause the substance to be paramagnetic, and probably colored.

The substance actually has a deep orange color at ordinary temperatures, suggesting the

* Contribution No. 387, Gates Chemical Laboratory.

[1] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, p. 80. Chemical Catalog Co., 1923.

[2] Pauling, J. Am. Chem. Soc. **53**, 1367 (1931); **53**, 3225 (1931).

[3] L. O. Brockway, Proc. Nat. Acad. Sci. **19**, 303, 868 (1933).

formula KO_2. In order to decide definitely between the two formulas, I undertook, at the suggestion of Professor Linus Pauling, the determination of the magnetic susceptibility. The substance was found to be paramagnetic, with a susceptibility corresponding to a Bohr magneton number of 2.04 at room temperature. This is close to the value 1.73 for the spin moment of one unpaired electron, and to the value 1.84 for a $^2\Pi$ molecule with doublet separation as in NO, as calculated by Van Vleck, the disagreement being explicable as resulting from experimental error or possibly from mutual interaction of the magnetic dipoles in the condensed phase. Hence we may say with confidence that the highest oxide of potassium has the formula KO_2. In view of this, the usual name potassium tetroxide seems unsatisfactory; at the suggestion of Professors W. C. Bray and E. D. Eastman of the University of California we propose that the substance be called potassium superoxide. The superoxide ion, $:\ddot{O}:\ddot{O}:^-$, occupies an intermediate position between the peroxide ion, $:\ddot{O}:\ddot{O}:^=$, and the normal oxygen molecule, $:O::O:$.

I am indebted to Professor Pauling for suggesting the investigation.

Experimental Part

Preparation of the oxide

Potassium superoxide was prepared by slow burning of potassium metal in incompletely dried oxygen at 300°. The apparatus used is shown diagrammatically in Fig. 1. About 15 g of potassium was first washed in ether to remove the oil from the surface. The apparatus was swept out with dry nitrogen after which the metal was placed in chamber *A*. The metal was then melted and filtered through the glass wool pad at the base of *A* into the vessel *C*, the volume of which was 50 cc. A slight pressure of nitrogen was found necessary to force the molten metal through the filter pad. The apparatus was next sealed at *B* and the metal slowly distilled into *E*. The distillation was carried out under reduced pressure and took place at about 200°. A portion of the distillate was retained in the tubes *F* for tests on the purity of the metal by means of magnetic measurements. When cool, the apparatus was placed under a slight pressure of nitrogen at *G*, the tubes *F* were then sealed off and the apparatus broken at *D*. The vessel *E* was then placed in a metal bath (m.p. 65°) and raised slowly to a temperature of 300°. At the same time a stream of nitrogen was passed through the apparatus, through *D*. Pure oxygen which was washed in concentrated sulfuric acid and passed through soda lime and calcium chloride in tubes 30 cm long was then gradually substituted for the nitrogen. The gas was passed slowly into the apparatus with constant heating for 50 hours. At the end of this time the potassium had been completely converted into the superoxide in the form of an orange powder. The product was allowed to cool in a stream of oxygen and the apparatus was finally sealed at *G* and *D*. Because of the great reactivity of the oxide with moisture and carbon dioxide in the atmosphere all subsequent manipulations of the compound were carried on in a "dry chamber." Even here the substance absorbed some moisture on standing more than an hour. The oxide was analyzed for alkali by titrating its aqueous solution with standard acid. The percent potassium was 1.8 percent higher than required by

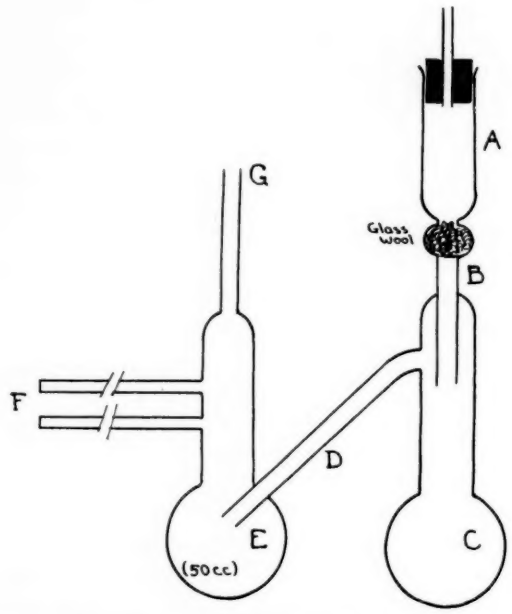

Fig. 1. Apparatus for distilling potassium and preparing potassium superoxide.

the formula K_2O_4 or KO_2; this discrepancy may be due to water absorbed during manipulations attendant on grinding and weighing the samples.

The behavior of the potassium during oxidation was the same as reported by Holt and Simms.[4] The oxygen used was dried as described above on the recommendation of these authors. They found that more thorough drying is undesirable since it becomes extremely difficult to burn potassium in extremely dry oxygen.

Magnetic measurements

The magnetic susceptibilities of the oxide, a sample of the metal from which it was prepared, and of an aqueous solution of the oxide were measured in the usual manner. A Sartorius micro-balance was used for the weighings. Acknowledgment is here made to Dr. Alfred Faessler of the Norman Bridge Laboratory of Physics for the kind loan of his apparatus.

The substances measured were enclosed in glass tubes 0.17 cm in diameter and with ends sealed off square. These tubes were sections from the same piece of glass tubing.

Potassium was found to be slightly paramagnetic, with a volume susceptibility of 0.40×10^{-6} at 21.5° in a field strength of 13,290 gauss. This is slightly lower than the value of 0.52×10^{-6} reported in the *International Critical Tables* and shows that the metal used was free from paramagnetic and ferromagnetic impurities.

Potassium superoxide was found to be paramagnetic. The volume susceptibility was 30.44×10^{-6} at 25.6° in a field strength of 8740 gauss. The effective Bohr magneton number was calculated from this to be 2.04 for the formula KO_2.

The aqueous solution of the oxide was slightly diamagnetic as would be expected of a pure solution of potassium hydroxide. This indicates that the paramagnetism exhibited by the oxide was inherent to the oxide and not to impurities. All of the values reported above have been corrected for the magnetic effects of the enclosing tubes.

[4] Holt and Simms, J. Chem. Soc. **T.** 432 (1894).

The Structure of the Hypophosphite Group as Determined from the Crystal Lattice of Ammonium Hypophosphite

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The crystal structure of ammonium hypophosphite was examined in order to determine the size and shape of the hypophosphite group. The crystals are orthorhombic-holohedral with the dimensions of the unit cell; $a=3.98$A, $b=7.57$A, $c=11.47$A. There are 4 molecules $NH_4(H_2PO_2)$ in the cell, and the space group is $Acmm(V_h^{21})$. The complete structure is given by the following parameter values: 4 N in $\pm(0\frac{1}{4}0)$, 4 P in $\pm(u_1 0\frac{1}{4})$ with $2\pi u_1=195°\pm5°$; 8 O in $\pm(u_2 0 v_2)$ with $2\pi u_2=125°\pm5°$ and $2\pi v_2=49°\pm2°$; 8 H in $\pm(u_3 v_3\frac{1}{4})$ with $2\pi u_3=290°$ and $2\pi v_3=51°$; 16 H in $\pm(xyz)$. The parameter values for phosphorus and oxygen were determined directly from the observed intensities of reflections, whereas the hydrogen values are based upon reasonable assumptions. The hypophosphite group has the shape of a distorted tetrahedron; two of the tetrahedral corners being occupied by oxygen atoms and the other two by hydrogen atoms. The phosphorus to oxygen distance is 1.51A and the angle between the phosphorus to oxygen bonds 120°. The distance from phosphorus to hydrogen is 1.5A and the angle between the P—H bonds 92°. Each ammonium radical is surrounded by four oxygen atoms at a distance of 2.81A and by four hydrogen atoms at a distance of 3.08A. There is strong indication that the ammonium radical is not rotating, and that hydrogen atoms of the NH_4-groups are linked to the surrounding oxygen atoms as well. The hydrogen atoms of the hypophosphite group behave toward ammonium as if they were H^- ions.

FOR a number of years one of us has been making systematic investigations with the purpose of determining the exact shape and dimensions of inorganic groups in crystals. With recent developments in the theory of chemical binding examinations of this kind get additional significance. The experimental data which are available concerning the structures of the oxygenic radicals of atoms in the first two rows of the periodic system are now fairly extensive, although far from complete. Notably the data on boron-oxygen and on phosphorus-oxygen groups are very few. Of the latter groups only the structure of the ortho-phosphate radical has been determined. It is the purpose of the present paper to describe the results of an investigation on the structure of the hypophosphite group.

The ammonium compound was chosen as suitable for the examination. The crystals were prepared for us through the kindness of A. E. Sidwell of the Jones Chemical Laboratory of this university. They conform to the description given by Groth[1] who reports them as orthorhombic bipyramidal with axial ratios: $a:b:c=0.5276:1:1.5137$. The density was determined by us with the suspension method and gave the value 1.634.

The x-ray data consisted of Laue and oscillation photographs. For the latter Mo K radiation was used. For the dimensions of the orthorhombic unit cell we found: $a=3.98$A, $b=7.57$A, $c=11.47$A —accuracy $\frac{1}{2}$ percent. By using the density given above, it is readily seen that the unit cell contains 4 molecules $NH_4H_2PO_2$. The space lattice is base centered since reflections were only observed from planes hkl for which $k+l$ is even. Furthermore, planes $0kl$ reflect only if k and l both are even, indicating that the space group is $Acmm(V_h^{21})$. It was a comparatively easy task to determine the distribution of the atoms among the available positions of the space group. We found:

4 N atoms in $\pm(0\frac{1}{4}0)$, $\pm(0\frac{3}{4}\frac{1}{2})$

4 P atoms in $\pm(u_1 0\frac{1}{4})$ $\pm(u_1\frac{1}{2}\frac{3}{4})$,

8 O atoms in $\pm(u_2 0 v_2)$, $\pm(u_2 0\frac{1}{2}-v_2)$,

$\pm(u_2\frac{1}{2}v_2+\frac{1}{2})$ $\pm(u_2\frac{1}{2}\bar{v}_2)$.

The hydrogen atoms have a negligible influence on the amplitude of the scattered radiation; their positions will therefore be discussed later.

[1] P. Groth, *Chemische Krystallographie*, Vol. 2, p. 770, Leipzig, 1908.

The determination of the three parameter values for phosphorus and oxygen entirely on the basis of the observed intensities of reflections presented no serious difficulties. The values are: $2\pi u_1 = 195° \pm 5°$, $2\pi u_2 = 125° \pm 5°$ and $2\pi v_2 = 49° \pm 2°$.

The good agreement between calculated amplitudes and observed intensities, to be seen in Tables I, II and III, constitutes the ultimate proof of the correctness of the parameter values for nitrogen, phosphorus and oxygen. The scattering powers for phosphorus and oxygen have been experimentally determined by J. West[2] for potassium dihydrogen-phosphate. The scattering power of nitrogen (or more correctly of the ammonium group) we assumed to be the same as for oxygen.

Two-thirds of the hydrogen atoms per unit cell are associated with nitrogen atoms to form the ammonium ions. These hydrogen atoms will be referred to as H_I atoms. The ammonium radicals may or may not be rotating in the crystal.

TABLE I. *Reflections 0kl.**

00*l*	sin θ/λ	*I*	*F*	02*l*	sin θ/λ	*I*	*F*	04*l*	sin θ/λ	*I*	*F*	06*l*	sin θ/λ	*I*	*F*
				020	0.132	vs	63	040	0.264	vs	69	060	0.396	w+	27
002	0.087	s	−18	022	.158	vs	−64	042	.278	w+	27	062	.405	w	−28
004	.174	m	10	024	.219	w+	−27	044	.316	w	10	064	.433	nil	−7
006	.262	vw−	3	026	.293	m	−24	046	.372	vw−	0	066	.475	vw	−16
008	.349	vs	48	028	.373	m	25	048	.437	ms	38				
00.10	.436	w+	−24	02.10	.455	m−	−32	04.10	.510	w−	−16				
00.12	.523	vw−	10	02.12	.540	nil	0								

TABLE II. *Reflections h0l.**

00*l*	sin θ/λ	*I*	*F*	10*l*	sin θ/λ	*I*	*F*	20*l*	sin θ/λ	*I*	*F*	30*l*	sin θ/λ	*I*	*F*
				100	0.127	s	−39	200	0.251	m	27	300	0.378	tr	16
002	0.087	s	−18	102	.153	vs	61	202	.266	vw	−5	302	.387	w	20
004	.174	m	10	104	.215	vw	13	204	.306	s	39	304	.415	w	−19
006	.262	vw−	3	106	.290	s	25	206	.363	w−	−9	306	.459	w+	24
008	.349	vs	48	108	.371	m	−18	208	.430	w+	17	308	.513	nil	6
00.10	.436	w+	−24	10.10	.454	m−	27	20.10	.503	nil	−3				
00.12	.523	vw−	10												

TABLE III. *Reflections hk0 and hkl.*

0*kl*	sin θ/λ	*I*	*F*	1*kl*	sin θ/λ	*I*	*F*	2*kl*	sin θ/λ	*I*	*F*	3*kl*	sin θ/λ	*I*	*F*	4*kl*	sin θ/λ	*I*	*F*
				100	0.127	m	−39	200	0.251	w+	27	300	0.378	tr	16	400	0.503	nil	3
011				111	.148	w+	−23	211	.263	nil	10	311	.385	vw−	9	411	.509	vw+	−18
020	0.132	s	63	120	.182	s+	−77	220	.284	vw−	−5	320	.400	vw	−4	420	.520	nil	−8
013				113	.193	m+	−27	213	.291	m	25	313	.404	w+	−14	413	.523	nil	8
022	.158	s	−64	122	.202	w+	11	222	.297	m	−31	322	.409	tr	1	422	.527	nil	−12
031				131	.239	vw+	−14	231	.323	nil	7	331	.428	vw	9	431	.542	vw−	−17
024	.219	w	−27	124	.252	m−	−27	224	.333	w	13	324	.436	w+	−35				
015				115	.260	w+	29	215	.339	m	−29	315	.440	w+	15				
033				133	.269	w−	−19	233	.346	w+	21	333	.445	w	−13				
040	.264	s−	69	140	.292	w+	−23	240	.364	w+	19	340	.460	nil	10				
042	.278	w	−13	142	.305	m−	35	242	.375	vw	−5	342	.468	vw	16				
026	.293	w+	−24	126	.319	vw−	2	226	.386	w+	−26	326	.477	vw−	9				
035				135	.320	w+	23	235	.387	w+	−25	335	.478	w−	14				
017				117	.337	tr	1	217	.401	tr	4	317	.489	vw+	−9				
044	.316	vw	10	144	.340	nil	6	244	.404	w+	30	344	.492	vw+	−16				
051				151	.356	nil	−8	251	.417	nil	4	351	.503	vw−	7				
053				153	.377	vw	−15	253	.435	vw+	17	353	.518	vw	−12				
037				137	.385	nil	−1	237	.442	vvw	4	337	.524	tr	−9				
046	.372	nil	0	146	.392	w	22	246	.449	vw	−9	346	.529	vw−	19				
028	.373	w+	25	128	.393	w+	−35	228	.450	tr	3	328	.530	nil	−6				
055				155	.415	vw−	16	255	.469	w−	−20	355	.546	vw	12				
060	.396	w+	27	160	.415	w+	−34	260	.469	nil	1	360							
019				119	.417	nil	−9	219	.471	nil	5	319	.548	vw−	6				
062	.405	w	−28	162	.424	vw	9	262	.477	vw	−19								
064	.433	nil	−7	164	.451	vw	−14	264	.500	vvw	10								
048	.437	w+	38	148	.455	w−	−14	248	.504	vw+	14								

* *I* = Observed intensity; *F* = calculated amplitude.

[2] J. West, Zeits. f. Krist. **74**, 306 (1930).

Each nitrogen atom is surrounded by four oxygen atoms at a distance of 2.81A. The four oxygen atoms form an almost regular tetrahedron around nitrogen, the angles between the connection lines N−O being 95°, 113° and 121°. This fact indicates rather strongly that the H_I atoms are linked to the oxygen atoms as well. We shall see later that considerations of the N−O distances support this view. Accordingly the ammonium groups are not rotating and the H_I atoms must be placed in general positions $\pm(xyz)$, etc., with such values of x, y and z as would place the hydrogen atoms somewhere along the connection lines N−O.

Now let us consider the remaining one-third of the hydrogen atoms in the unit cell. These atoms we will refer to as H_{II}. Two possibilities will be considered: (1) $NH_4H_2PO_2$ is a true acid salt (2) the hypophosphite radical is $(H_2PO_2)^-$ with the two hydrogens attached directly to phosphorous. Of course, the chemists have accepted the latter possibility as the correct one, because of the mono-basic character of the hypophosphorous acid. However, we found it to be of interest to disprove case 1 by direct evidence.

We know the crystal lattice of two acid salts (KH_2PO_4 and $NaHCO_3$) and of one acid (H_3BO_3) with great accuracy. The hydrogen atoms are in every case attached to two oxygen atoms forming collinear groups O−H−O with an O−O distance of 2.55A or 2.71A(H_3BO_3). Obviously this is the characteristic feature of crystalline oxygenic acids and acid salts. Now in the present crystal the closest distance between two oxygen atoms (which are attached to different phosphorus atoms) is 3.45A. Consequently there is no possibility for having an O−H−O group of the proper size, and $NH_4H_2PO_2$ is not to be termed an acid salt.

In agreement with chemical evidence we are therefore led to believe that the H_{II} atoms are attached directly to phosphorus.

It is reasonable to suppose that the four bonds of phosphorous are directed more or less toward the corners of a tetrahedron. This means that the H_{II} atoms are lying in positions $\pm(u_3v_3\frac{1}{4})$, $\pm(\bar{u}_3, \frac{1}{2}-v_3, \frac{1}{4})$, $\pm(\bar{u}_3, v_3+\frac{1}{2}, \frac{1}{4})$, $\pm(u_3, \bar{v}_3, \frac{1}{4})$. Assuming a distance of 1.50A for phosphorus to hydrogen, the ammonium to hydrogen distance becomes about 3.1A. This indicates a binding between NH_4 and H_{II}, so that an H_{II} atom is linked to one phosphorus atom and two ammonium groups. It is logical to assume that these three bonds from hydrogen (to one P and two NH_4) are lying in one plane. This latter assumption together with the assumed P−H distance of 1.50A fix completely the positions of the H_{II} atoms. The parameter values become: $2\pi u_3 = 290°$; $2\pi v_3 = 51°$.

It now remains to be seen if our assumptions lead to a reasonable structure for the hypophosphite group. (It should be emphasized that the phosphorus and oxygen positions were determined directly from the observed intensities of reflections.) Phosphorus is linked to two oxygen atoms at a distance of 1.51A with a maximum error of 0.11A. The angle between the P−O bonds is 120° with a maximum error of 8°. The oxygen to oxygen distance is 2.61A. With the accepted H_{II} parameters one finds the angle between the P−H bonds to be 92°, while the angle between a P−O and a P−H bond becomes 117°. This is a reasonable result: In replacing two of the oxygen atoms in the PO_4-group by hydrogen atoms it is to be expected that the initial tetrahedral angles between bonds will be modified. On general grounds the repulsion between two oxygen atoms (not linked together) must be greater than between an oxygen and a hydrogen atom, and this again greater than for two hydrogen atoms. Hence we should expect the angle between the P−O bonds to be greater than the tetrahedral angle, the angle between the P−H bonds to be less than the tetrahedral angle. The H−H distance in the group is 2.16A and the H−O distance 2.45A.

Around each ammonium group there are four oxygen atoms at a distance of 2.81A and there are four H_{II} atoms at a distance of 3.08A. The coordination number thus is 8. The crystal radius of the rotating ammonium ion is 1.44A.[3] The calculated NH_4−O distance for coordination number 8 (reference 3) is 3.02A, which is considerably higher than the observed value of 2.81A. The difference is far greater than can be accounted for by the approximation involved in the conception of ionic radii. It is logical to attribute the cause of the discrepancy to a non-

[3] W. H. Zachariasen, Zeits. f. Krist. **80**, 137 (1931).

rotating ammonium group, i.e., that the observed distance of 2.81 refers to the N−O distance in group N−H−O, rather than to (NH_4)−O. It is to be recalled that the presence of nonrotating ammonium radicals was made plausible also by another observation.

It is a well-known fact, tested by scores of observations, that the oxygen atoms in oxygenic radical ions (as $(CO_3)^{-2}$, $(NO_3)^{-}$, $(SO_4)^{-2}$, $(ClO_4)^{-}$, $(ClO_3)^{-}$) behave as O^{-2} ions at least with respect to the cations linking the radicals together. We may try if the same applies to the hydrogen atoms in the hypophosphite group. That is to say: Will the H_{II} atoms behave as H^{-} ions with respect to the (NH_4) ions? From the recent data on the structure of the alkali hydrides[4] we deduce a radius of 1.52A for H^{-}. With this value we calculate an $(NH_4)^{+}-H^{-}$ distance of 3.09A (for coordination number 8), while the observed value was 3.08A.

Indeed the conception of ions permits fairly accurate predictions of interatomic distances even in radicals, where the binding only in part is ionic. Thus we may think of the hypophosphite radical as consisting of ions: $(H_2^{-}P^{+5}O_2^{-2})^{-}$. The crystal radii of these ions are all known (reference 3) so that we may calculate the interionic distances. We find 1.56A and 1.48A for $P^{+5}-O^{-2}$ and $P^{+5}-H^{-}$, respectively, while we observed 1.51A for P−O and assumed 1.50A for P−H.

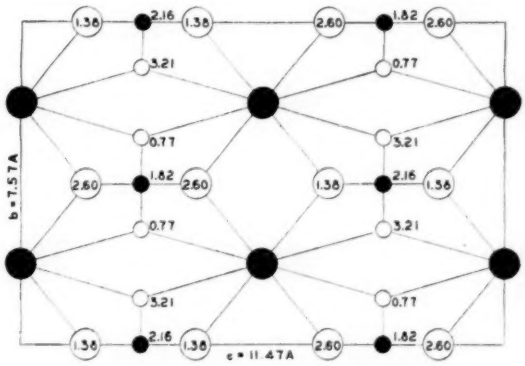

FIG. 1. The drawing shows the structure projected on the *a*-face. Large filled circles represent ammonium groups, small filled circles phosphorus atoms. Large open circles represent oxygen atoms, while the small open circles represent the hydrogen atoms (H_{II}). The ammonium groups all lie in the plane of the paper. The attached numbers indicate for the other atoms their height in A above the plane of the paper. Bonds are indicated by connection lines.

[4] E. Zintl and A. Harder, Zeits. f. physik. Chemie **B14**, 265 (1931).

On the States of Aggregation

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The problem of investigating systematically the possible states of aggregation has not yet been attacked. It has been approached here in the hope of getting a deeper insight into the nature of the liquid state. After a discussion of the general methods, a simplified one-dimensional model is introduced. It was possible to find the exact equation of state. However, it turned out that in this case a single (gaseous) state exists. This is due to the presence of aggregates of all sizes. It is found that the existence of at least one condensed state is possible only if the change in free energy that occurs when an atom is added to a large aggregate is higher than the change that occurs in the addition of this atom to a small molecule. No progress could be made in the understanding of the liquid state.

I. INTRODUCTION

IN attempting to obtain some insight into the nature of the liquid phase,[1] we were struck by the absence of a general method of investigating which states of aggregation are possible.

If we know all the properties of an isolated molecule, but had never experienced matter in bulk, we might have predicted theoretically a state of low density and complete disorder, the gas, and also perhaps a state of high density and perfect geometrical order, the crystal.

Historically the van der Waals equation is an attempt to explain the existence of the liquid phase, but gives no account of the solid state.

In this paper, an endeavor was made to deduce exactly the general equation of state under simplified assumptions concerning the molecular interaction.

II. GENERAL THEORETICAL CONSIDERATIONS

Thermodynamically, the free energy F as a function of volume and temperature determines the properties of the substance. The pressure is obtained from the equation $p=-\partial F/\partial v$. To determine the number of states of aggregation possible at a given temperature, one follows the isotherm $p(V)$ at constant temperature. At transitions between two phases one of two phenomena may occur. Either there are no metastable states, in which case the isotherm should be horizontal at the transition pressure (vapor pressure or pressure of fusion) between the specific volumes of the two phases; or if there are metastable or unstable phases possible between the two phases (van der Waals equation), the pressure curve should have a maximum and minimum.

The kinetic theory then should provide a method for the deduction of the isotherms in the whole volume-range. Provided we remain in the region of classical physics, the volume-dependent part of the free energy of N identical molecules is given by the phase integral:

$$\Phi=e^{-F/kT}$$

$$=\frac{1}{N!}\int\cdots\int e^{-E/kT}dx_1dy_1\cdots dx_Ndy_Ndz_N. \quad (1)$$

Here $x_ny_nz_n$ are the coordinates of the nth molecule, while $E(x_1\cdots z_N)$ is the mutual potential energy of the molecules in a given position. The integral is to be extended up to the walls of the vessel.

This method, however, seems not to lead to metastable states. The pressure deduced from Φ is the weighted average for all states possible at a given volume and temperature. Now metastable states are, of course, states that will occur very rarely in the course of events. For example, if we have a vessel almost filled with a liquid, while the rest of the volume is filled with vapor, we have a possible metastable state, in which the whole material is in the liquid state, but the liquid is adhering everywhere to the walls under a nega-

[1] See also J. A. Prins, Naturwiss. 19, 435 (1931), O. Kratky, Phys. Zeits. 34, 482 (1933).

tive pressure. Now it is quite clear that the probability of this state is very small, as it will happen exceedingly rarely that the liquid in the almost filled vessel suddenly expands through Brownian motion, and fills the vessel completely. Therefore the average properties given by the phase integral will be the properties of the normal state and we should, from its use, always get curves of the type described in the first alternative. We do not know of any general statistical method that would give us the metastable states. The difficulty consists, of course, in the lack of a sharp definition of a state, except by the external variables, volume and temperature.*

Tammann[2] has adduced reasons against the possibility of a continuity between the liquid and crystalline states. However, from the standpoint of general statistical mechanics, which we have described here, we cannot see any objections against the postulate to find all the possible states, including the crystalline, from a single formula, like formula (1). It might be that Tammann's objections are taken care of by the absence of the metastable states, and their replacement by a sharp break in the isotherm, as described above. We have not succeeded in actually evaluating the phase integral, except in a very simplified case, which will now be treated.

III. Simplified One Dimensional Model

We consider N molecules which can move in a straight line over a distance L. If each molecule has a diameter d, the free space is $L-N\,d=V$, and everything will behave as if we had point molecules in a line of length V. We make the assumption that only neighboring molecules act on each other. Their interaction energy ϵ_ν depends on the distance between them. If x_ν denotes the coordinate of the νth molecule, and if we further assume that also the origin (the wall at the left) behaves like a molecule and exerts the potential energy $\epsilon(x_1)$ the total energy E becomes

$$E=\epsilon(x_1)+\epsilon(x_2-x_1)+\epsilon(x_3-x_2)+\cdots+\epsilon(x_N-x_{N-1}).$$

The integral (1), which takes the form[3]

$$\Phi=\int_0^V dx_1\int_{x_1}^V dx_2\cdots\int_{x_{N-1}}^V dx_N e^{-E/kT}$$

can be transformed by introducing the mutual distances

$$\zeta_1=x_1,\qquad \zeta_2=x_2-x_1\cdots,\qquad \zeta_N=x_N-x_{N-1}$$

into

$$\Phi=\int_0^V e^{-\epsilon_1/kT}d\zeta_1\int_0^{V-x_1} e^{-\epsilon_2/kT}d\zeta_2\cdots\int_0^{V-x_{N-1}} e^{-\epsilon_N/kT}d\zeta_N. \quad (2)$$

It is simpler not to express x by ζ in the upper limit. We now assume ϵ_n to have the simplest form; that is

$$\epsilon_n=-\epsilon \qquad \zeta_n<r_0,$$
$$\epsilon_n=0 \qquad \zeta_n>r_0,$$

so that the total energy curve is given by Fig. 1.

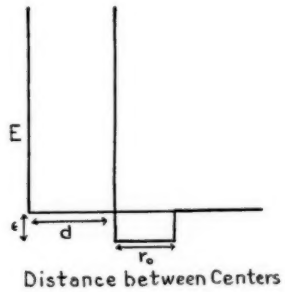

Fig. 1. Mutual potential energy of two molecules.

The formula is evaluated in Appendix I. The result is, with the abbreviation $e^{\epsilon/kT}=a$: For $V>Nr_0$

$$\Phi=\frac{1}{N!}\sum_0^N\binom{N}{\lambda}(1-a)^\lambda a^{N-\lambda}(V-\lambda r_0)^N. \quad (3)$$

For $V<Nr_0$ we define N' through $N'r_0<V<(N'+1)r_0$ and find

$$\Phi=\frac{1}{N!}\sum_0^{N'}\text{same expression}. \quad (3')$$

* *Added in Proof:* The problem has been solved by Professor Otto Stern during a conversation. He pointed out that the portion of the phase space belonging to the metastable state must be surrounded by a potential barrier calculated per molecule high compared with kT.

[2] G. Tammann, *Aggregatzustände*, p. 41, Leipzig, 1922.

[3] $N!$ has been left out in the denominator because there is no exchange of particles possible here.

For $V<r_0$ this becomes

$$\Phi=(aV)^N/N!. \tag{3''}$$

These formulae are exact.

For very large volumes we find of course

$$\Phi=(1/N!)\,V^N,$$

which is the formula of the ideal gas (with finite molecules). We have the same formula, only with the addition of a potential energy ϵ, also in case (3'').

We might expect equilibrium between gas and a condensed phase in the following region: T a fraction of $(N\epsilon/R)$ ($N\epsilon$ the heat of evaporation), the volume in the interval between the volume of the saturated vapor, that is $V\sim Nr_0e^{\epsilon/kT}$, down to the volume of the condensed phase.

The formula (3) has been evaluated for this region in which $(1/a)=e^{-\epsilon/kT}$ is small, in Appendix II. The result is: Define x and y through[4]

$$x=(r_0N/V)a, \tag{4}$$

$$(x/y)(1-y)^2=1. \tag{5}$$

Then for large numbers of molecules N

$$\Phi^{1/N}=e^{-F/NkT}=(Ve/N)[e^{-y}/(1-y)^2]. \tag{6}$$

To calculate the equation of state, we form

$$\begin{aligned}\frac{p}{RT}&=-\frac{\partial}{\partial V}\frac{F}{NkT}=+\frac{\partial}{\partial V}\ln\Phi^{1/N}\\&=\frac{1}{V}-\frac{d}{dy}[y+2\ln(1-y)]\frac{dy}{dx}\frac{dx}{dV}\\&=\frac{1}{V}-\left(1-\frac{2}{1-y}\right)\frac{dy}{dx}\frac{dx}{dV}\\&=\frac{1}{V}+\frac{y}{x}\frac{dx}{dV}=\frac{1}{V}(1-y).\end{aligned} \tag{7}$$

Now from (5)

$$1-y=(1/2x)[(1+4x)^{\frac{1}{2}}-1]$$

or

$$\frac{p}{RT}=\frac{1}{2ar_0N}\left[\left(1+\frac{4ar_0N}{V}\right)^{\frac{1}{2}}-1\right]. \tag{7'}$$

[4] x is essentially the ratio of the saturation volume to the volume V.

It is clear that this formula does not show any region where p is independent of V (nor any maxima or minima). Accordingly, there are no transition points, i.e., there exists only a single phase.

Recently N. Fuchs[5] has investigated the adsorption-isotherm assuming that the adsorption occurred on a one dimensional system (edge) and that the adsorbed particles vibrated around fixed points of the adsorbing substance. He found, in agreement with our result, no break in the isotherm, that is, no phase change in the adsorbed substance.

It is possible to get a deeper understanding of this result.

Formula (7) can namely be interpreted in a different manner. Consider a group of n particles where each particle is within the reach of the potential energy of both neighbors (except the end particles which have only one neighbor) as a molecule of n atoms. Then we can consider the whole system according to the formulas which govern in statistical mechanics the chemical equilibrium between Z_1 atoms, Z_2 diatomic molecules, Z_n n-atomic molecules, etc.

We have

$$(Z_n\cdot Z_1)/Z_{n+1}=(V/r_0)e^{-\epsilon/kT}, \tag{8}$$

$$\sum_1^N nZ_n=N. \tag{9}$$

From (8) and (4) one finds

$$Z_n=Z_1{}^n(e^{\epsilon/kT}r_0/V)^{n-1}=Z_1(Z_1x/N)^{n-1}. \tag{10}$$

If we insert (10) in (9) we get, with the abbreviation $y'=Z_1x/N$,

$$\frac{1}{x}-y'\frac{1-Ny'^{N-1}+(N-1)y'^N}{(1-y')^2}=1. \tag{11}$$

This is replaced with sufficient accuracy[6] by

$$y'/x(1-y')^2=1. \tag{11'}$$

Comparison of (11') and (5) shows $y=y'$. The

[5] N. Fuchs, Zeits. f. physik. Chemie **B21**, 235 (1933).

[6] From (9) and (10) it follows that y' increases with x. If x is very small, y' is small, and the transition from (11) to (11') is clear. If x is large, y' is nearly 1, although for very large values of x (11') does not give the very small value $1-y'$ accurately.

pressure of the mixture of molecules of all sizes is

$$\frac{p}{RT}=\frac{1}{VN}\sum Z_n=\frac{1}{Vx}\sum_1^N y^n=\frac{1}{V}\frac{y}{x}\frac{1-y^N}{1-y}=\frac{1}{V}(1-y)$$

with the help of (5), again neglecting y^N in comparison with (1). But this formula is identical with (7). The reason, therefore, why we do not get a break in the isotherm is as follows: with changing volume the relative numbers of each type of molecule (there are N such types) change in a continuous manner which smoothes out the curve.

IV. Conditions for the Existence of a Condensed Phase

To get a separate phase it is necessary to make the large aggregates more probable compared with molecules containing only a few atoms.

To investigate that in more detail we can now make use of the usual dissociation formulae since their agreement with the exact calculation has been shown in the previous case.

As the simplest assumption we will permit the existence only of aggregates having at least m atoms, besides free single particles. Let the equations be[7]

$$Z_1{}^m=Z_mK_m{}^{-1},$$

$$Z_1Z_n/Z_{n+1}=N/x, \qquad N\geqq n>m.$$

Then $Z_n=Z_m(Z_1x/N)^{n-m}=K_m(N/x)^m(Z_1x/N)^n$

and

$$Z_1+K_m\left(\frac{N}{x}\right)^m\sum_m^N n(Z_1x/N)^n=N$$

or with the abbreviations $K_m(N/x)^{m-1}=A$, $Z_1x/N=y$.

$$y+A\sum_m^n ny^n=x$$

or

$$y\left[1+A\frac{my^{m-1}-(m-1)y^m-Ny^{N-1}+(N-1)y^N}{(1-y)^2}\right]=x.$$

For small values of x, we have simply $y=x$, or $Z_1=N$ and that is true almost up to $x=1$, as any appreciable deviation of y from 1 makes y^{m-1} very small for large m. For example, for $m=1000$ $1-x=0.02$ still leaves $y=x$ for $A\sim 1$, as before. For large x, putting $y=1-\delta$, we have $me^{-\delta m}/\delta=x$. The pressure equation is

$$\frac{p}{RT}=\frac{1}{VN}\left(Z_1+\sum_m^N Z_n\right)=\frac{1}{Vx}\left(y+A\sum_m^N y^n\right)$$

$$=\frac{1}{Vx}y\left(1+\frac{y^m-y^N}{1-y}\right).$$

Again we have for small values of x the gas equation, for large values

$$\frac{p}{RT}=\frac{1}{Vx}\left(1+\frac{e^{-\delta m}}{\delta}\right)=\frac{e^{-N\epsilon/RT}}{Nr_0}\left(1+\frac{x}{m}\right),$$

which is practically independent of V as long as $x\ll m$ or the volume larger than $1/m$ of the volume of the saturated vapor.

The foregoing assumption which forbids the existence of molecules containing more than 1 and less than m atoms is of course not realized in nature. The strong influence of the intermediate molecules in the model discussed in III is due to the fact that the right side of (8) is independent of n. That means thermodynamically that the change in free energy when an atom joins a molecule already containing n atoms is independent of n. To favor large molecules we must make the change larger for large n. This can be accomplished either by a larger change in energy or a smaller change in entropy.

In the model of III the change in energy is independent of n because in a one dimensional system one has to break only one bond to free an atom whatever the size of the molecule to which it is attached. In two or more dimensions that is different. We know experimentally that condensed phases exist in films in spite of the fact that if the molecules of these films vibrate around fixed points on the absorbing substance, the change of entropy is independent of n (see below). But in a two dimensional film the tearing loose of a molecule means the breaking of two bonds, if it is attached to a large mass, but only the breaking of one bond in the case of a small molecule.

[7] See also similar calculations by L. Michaelis, Biochem. Zeits. **103**, 225 (1920).

In three dimensions the difference is even greater. However, we have not yet succeeded in formulating this statement exactly.

The changes in entropy are essentially determined by the factor occurring in front of the e power in (8). In the model treated under III, the space available to the bound atom is r_0 independent of n, the number of atoms in the molecule. The same is true if (as in Fuchs' assumption) the vibrations are determined by the adsorbing substance. If we assume, however, that the particles in the aggregate vibrate in respect to each other instead of in respect to a fixed point in space, we get even in the one dimensional case a larger entropy per atom for the larger aggregate, because the average frequencies in a large aggregate are lower than in a small one.

The frequencies of a molecule of n particles are given approximately by $\nu=\nu_0/s$, $1<s<n-1$. Therefore, in the phase integral of the molecule there appears the factor[8]

$$\prod_s \frac{1}{\nu_s} = \frac{(n-1)!}{\nu_0{}^n}.$$

The dissociation formula takes the form

$$\frac{Z_1 Z_n}{Z_{n+1}} = V\frac{\nu_0}{n}\left(\frac{2\pi m}{kT}\right)^{\frac{1}{2}} e^{-\epsilon/kT}.$$

The essential thing is the n in the denominator which arises from the fact that the frequency which disappears through the removal of one atom is inversely proportional to the size of the molecule. Therefore, with the abbreviation

$$x' = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{N}{\nu_0 V} e^{\epsilon/kT},$$

we find

$$Z_n = (n-1)!\, Z_1 \left(\frac{Z_1 x'}{N}\right)^{n-1},$$

(9) takes the following form, with $y' = Z_1 x_1'/N$

$$\sum_1^N n!\, y'^n = x'. \tag{9'}$$

Furthermore, the pressure equation

$$pV/RT = \sum Z_n = (y'/x')N\sum (n-1)!\, y'^{n-1}$$
$$= (y'/x')N(1+x'-N!\, y'^N)$$

with the use of (9'). Now (9') shows for $x' \ll N^{-1}$ $y=x$, $pV=NkT$, ideal gas

$$x' > e/N \qquad y'^N = x'/N!, \qquad y' = e/N.$$

Therefore $pV/RT = e/x'$

$$p = \nu_0 (2\pi mkT)^{\frac{1}{2}} e^{-\epsilon/kT}$$

which is independent of V and is the correct vapor pressure equation for a one dimensional system.

Appendix I

One can easily interpret the integral (2). Consider an N-dimensional corner, formed by the positive axes $\zeta_1, \zeta_2 \cdots \zeta_N$ and limited by the plane which cuts the axis at $\zeta_j = V (j = 1 \cdots N)$. That is the domain of integration. The integrand is $\Pi e^{-\epsilon_j/kT}$, where ϵ_j depends only on ζ_j. Call

$$e^{\epsilon/kT} = a > 1. \tag{11}$$

The integrand has then the following property:

It is $=1$, if all the $\zeta > r_0$, that is to say in an inner N-dimensional pyramid of edge $V - r_0$.

It is a if one of the ζ is smaller than r_0 and all others larger than r_0, a^2 if two of the ζ are smaller than r_0 and all others larger, etc., finally the integrand is a^N in the cube of side r_0.

To give a better idea, consider a system containing only two particles. The configuration space is there two dimensional and has the form of a right-angle triangle, with sides $= V$. (Fig. 2.) It is divided into four parts: in A both $\zeta_1 = x_1$ and $\zeta_2 = x_2 - x_1$ are larger than r_0, both particles are free, the integrand has the value $1 (E = 0)$.

In B ζ_1 is smaller than r_0, ζ_2 larger than r_0, that is particle 1 is frozen to the wall, 2 is free, $\epsilon_1 = \epsilon$; $\epsilon_2 = 0$, the integrand is a. In C, $\zeta_1 > r_0$, $\zeta_2 < r_0$, the particles 1 and 2 stick together (form a molecule)

[8] See, e.g., K. F. Herzfeld, *Kinetische Theorie der Wärme*, Braunschweig (1925).

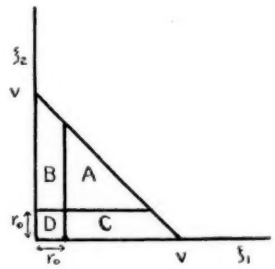

FIG. 2. Configuration plane for two molecules.

but are free from the wall, $\epsilon_1=0$, $\epsilon_2=\epsilon$, the integrand is again a. In D finally both ζ_1 and ζ_2 are smaller than r_0, particle 1 sticks to the wall, particle 2 sticks to particle 1, $\epsilon_1=\epsilon_2=\epsilon$, the integrand is a^2.

In general, it is evident that the integrand of (1) can only have the values a^l, with $l=0\cdots N$. Assume at first $V>Nr_0$. Then all values actually occur. The problem is equivalent to finding the volume of the phase space for which the integrand has the value a^l, subject to the condition $\sum_m \zeta_m < V$.

It is readily seen that this part of the phase space consists of $\binom{N}{l}$ unconnected, equally large regions, namely the $\binom{N}{l}$ possible combinations in which l coordinates are smaller, the others larger than r_0. It is therefore sufficient to find for each l the volume of the special region, A_l, for which only the *first* l coordinates ζ are smaller than r_0. Then

$$\Phi=\sum_l \binom{N}{l} a^l A_l. \tag{2I}$$

The volume A_l is given by the integral

$$A_l=\int_0^{r_0} d\zeta_1 \int_0^{r_0} d\zeta_2 \cdots \int_0^{r_0} d\zeta_l \int_{r_0}^{V-(N-l+1)r_0-\Sigma_{m=1}^{l}\zeta_m} d\zeta_{l+1}\cdots \int_{r_0}^{V-r_0-\Sigma_{m=1}^{N-2}\zeta_m} d\zeta_{N-1} \int_{r_0}^{V-\Sigma_{m=1}^{N-1}\zeta_m} d\zeta_N. \tag{3I}$$

Integration leads to

$$A_l=\int_0^{r_0} d\zeta_1 \cdots \int_0^{r_0} d\zeta_l [1/(N-l)!]\left\{ V-(N-l)r_0-\sum_{m=1}^{l}\zeta_m \right\}^{N-l} \tag{3'I}$$

and finally to

$$A_l=(1/N!)\sum_{m=0}^{l}(-1)^m \binom{l}{m} \{ V-(N-l+m)r_0 \}^N. \tag{4I}$$

In the case that $V<Nr_0$ we can define N' such that

$$N'r_0<V<(N'+1)r_0. \tag{5I}$$

It is evident then that because of the limitation $\sum_m \zeta_m \leqq V$ no more than $N-N'$ coordinates ζ_m can be $>r_0$ at the same time, the integrand can only take values a^l with $l \geqq N-N'$ or

$$A_l=0 \qquad \text{for} \qquad l<N-N'. \tag{4aI}$$

For $l>N-N'$ (3I and 3'I) are modified by the fact that the upper limit of the first l integrals is no more simply r_0, but has to be replaced (for the kth integral) by the smaller of the two numbers r_0

or $V-(N-k)r_0-\sum_{m=0}^{k-1}\zeta_m$. Then integration leads to

$$A_l=\frac{1}{N!}\sum_{m=0}^{l-(N-N')}(-1)^m\binom{l}{m}\{V-(N-l+m)r_0\}^N. \tag{4bI}$$

If for $V=Nr_0$ we define N' as $N=N,'$ (4I) is contained in (4bI).

Introducing the label λ for $N-l+m$, (4bI) reads

$$A_l=\frac{1}{N!}\sum_{\lambda=0}^{N'}(-1)^{N+l+\lambda}\binom{l}{N-\lambda}(V-\lambda r_0)^N. \tag{6I}$$

Formally the sum runs only from $N-l$ to N', but the factorial coefficient renders the lower terms 0. Φ is obtained by putting (6I) and (4aI) into (2I). Exchanging the order of the summation we obtain

$$\Phi=\frac{1}{N!}\sum_{\lambda=0}^{N'}(-1)^\lambda\frac{N!}{(N-\lambda)!\lambda!}(V-\lambda r_0)^N\sum_{l=N-N'}^{N}(-1)^{N-l}\frac{\lambda!}{(N-l)!(\lambda-N+l)!}a^\lambda.$$

Since $N-N'<\lambda$ the second sum is simply the expression $a^N(1-1/a)^N$ and the final result is:

$$\Phi=\frac{1}{N!}\sum_{\lambda=0}^{N'}\binom{N}{\lambda}(1-a)^\lambda a^{N-\lambda}(V-\lambda r_0)^N. \tag{7I}$$

Appendix II

For $-\epsilon/kT>1$, $a\gg1$, one can write in (3)

$$(1-a)^\lambda a^{N-\lambda}=a^N(1/a-1)^\lambda=(-1)^\lambda a^N e^{-(\lambda/a)}.$$

Furthermore develop

$$(V-\lambda r_0)^N=V^N(1-\lambda r_0/V)^N=V^N\sum_0^N(-1)^j\lambda^j(r_0/V)^j\binom{N}{j}$$

and interchange the order of summation in respect to λ and j. Then (3) takes the form

$$\Phi=(a^N/N!)V^N\sum_{j=0}^{N}\binom{N}{j}(-1)^j(r_0/V)^j\sum_{j=0}^{N}\binom{N}{\lambda}(-1)^\lambda\lambda^j e^{-(\lambda/a)}$$

$$=(a^N/N!)V^N\sum_{j=0}^{N}\binom{N}{j}(r_0/V)^j[d^j/d(1/a)^j]\sum_{\lambda=0}^{N}(-1)^\lambda\binom{N}{\lambda}e^{-(\lambda/a)}$$

$$=(a^N/N!)V^N\sum_{j}\binom{N}{j}(r_0/V)^j[d^j/d(1/a)^j](1-e^{-(1/a)})^N$$

$$=(a^N/N!)V^N\sum_{j}\binom{N}{j}(r_0/V)^j[d^j/d(1/a)^j](1/a)^N$$

$$=\frac{V^N}{N!}\sum_{j=0}^{N}\binom{N}{j}\frac{N!}{(N-j)!}\left(\frac{r_0a}{V}\right)^j=\frac{V^N}{N!}\sum_{j=0}^{N}\binom{N}{j}\frac{N!}{(N-j)!N^j}\left(\frac{r_0Na}{V}\right)^j. \tag{1II}$$

Introduce the abbreviation x according to (4). The limits of x are $x=0$ for $V=\infty$; $x=a\gg 1$ for $V=r_0N$. Consider first $(A+B)!$ for $A\gg B\gg 1$. We have according to Stirling's formula

$$\ln (A+B)!=(A+B)[\ln (A+B)-1]-\ln [2\pi(A+B)]^{\frac{1}{2}}$$
$$=(A+B)[\ln A-1+\ln (1+B/A)]-\ln [2\pi(A+B)]^{\frac{1}{2}}.$$

Up to and including terms in $(B/A)^2$, we have $\ln (1+B/A)=B/A-B^2/2A^2$. Therefore

$$\ln (A+B)!=(A+B)[\ln A-1]+B\left(1+\frac{1}{2}\frac{B}{A}\right)-\ln [2\pi(A+B)]^{\frac{1}{2}}. \tag{2II}$$

Let us call j_0 the value of j that gives the largest term in (1II), and $\xi=(j-j_0)/j_0$, $j=j_0(1+\xi)$. One can write then

$$\ln\left\{\binom{N}{j}\frac{1}{(N-j)!\,N^j}x^j\right\}=\ln N!-\ln (j_0+j_0\xi)!-2\ln [N-j_0-j_0\xi]!+j_0(1+\xi)\ln\frac{x}{N}$$
$$=\ln N!-j_0(1+\xi)[\ln j_0-1]-j_0\xi(1+\xi/2)-2(N-j_0-j_0\xi)[\ln (N-j_0)-1]!$$
$$+2j_0\xi(1+\tfrac{1}{2}j_0\xi/(N-j_0))+j_0(1+\xi)\ln (x/N)+\tfrac{1}{2}\ln [8\pi^3(N-j_0)^2j_0]$$
$$=\ln N!+j_0\left[\ln\frac{x(N-j_0)^2}{Nj_0}-1\right]-2N[\ln (N-j_0)-1]+j_0\xi\ln\frac{x(N-j_0)^2}{Nj_0}$$
$$-(j_0/2)\xi^2[1+2j_0/(N-j_0)]+\tfrac{1}{2}\ln [8\pi^3(N-j_0)^2j_0]$$
$$=-\ln N!-2N\ln\left(1-\frac{j_0}{N}\right)+j_0\ln\frac{x(N-j_0)^2}{Nj_0}-j_0+j_0\xi\ln\frac{x(N-j_0)^2}{Nj_0}$$
$$-(j_0/2)\xi^2(N+j_0)/(N-j_0)+\tfrac{1}{2}\ln [8\pi^3(N-j_0)^2j_0]. \tag{3II}$$

The maximum occurs for $x(N-j_0)^2/Nj_0=1$, or if we call $j_0/N=y$,

$$(x/y)(1-y)^2=1. \tag{4II}$$

We have then

$$\Phi=[8\pi^3(N-j_0)^2j_0]^{\frac{1}{2}}\frac{V^N}{N!}\frac{e^{-Ny}}{(1-y)^{2N}}\sum\exp\left(-\frac{Ny}{2}\frac{1+y}{1-y}\xi^2\right). \tag{5II}$$

Instead of taking the sum, one can write an integral, introducing $u^2=(Ny/2)[(1+y)/(1-y)]\xi^2$. The limits, being given by $j=0$ and $j=N$ or $u=-[(Ny/2)(1+y)/(1-y)]^{\frac{1}{2}}$ and $u=[N(1-y^2)/2y]^{\frac{1}{2}}$, can be replaced by $-\infty$ and ∞. Therefore

$$\Phi=4\pi^2N(1-y)\left(\frac{1-y}{1+y}\right)^{\frac{1}{2}}\frac{V^N}{N!}\frac{e^{-Ny}}{(1-y)^{2N}}$$

and if we take the Nth root formula (6) is found.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Carbon-Halogen Bond Energy and the Molecular Structure as Related to Halogen Alkyls

The purpose of the work described here was to determine the modification of the characteristics of the bond between the carbon and halogen atom, that is, (1) the effect of the halogen substitution for another halogen atom or hydrogen atom, (2) the effect of a lengthening of the hydrocarbon chain, and (3) the effect of a branching of the hydrocarbon chain upon the carbon-halogen bond.

In recent years a continuous absorption spectrum which corresponds to the immediate dissociation of the molecule into its constituents was investigated of a number (about 50) of halogen alkyls[1] both in the liquid and in the vapor state in the ultraviolet region. The energy of dissociation of the carbon-halogen bond was, in each case, estimated from absorption edge. The data of results obtained are not so accurate as the absolute values, but they seem to have a definite physical meaning as relative values and to be of sufficient interest to warrant publication. Some remarkable facts revealed by the data obtained are briefly summarized as follows.

(1) It is obvious, in any case of halogen alkyls, from the results of many sequences of compounds that the energy of the carbon-halogen bond increases rapidly from iodide to bromide to chloride, that is, with the decreasing of atomic weight.

(2) The carbon-halogen bond energy decreases successively as the hydrogen atom is substituted by the halogen atom in any case of halogen alkyls. So it has the maximum value for monohalogen compound as shown in Table I.

(3) The carbon-halogen bond energy is modified more or less as the length of the hydrocarbon chain is varied. It seems that the bond energy increases on the whole as the length of the CH_2 group is increased as shown in Table II.

TABLE I.

Molecules	Diss. energy (kcal./mol)
CCl_4	117.1
$CHCl_3$	121.3
CH_2Cl_2	123.4
CH_3Cl	124.5

TABLE II.

Molecules	Diss. energy (kcal./mol)
CH_3Br	96.4
$n-C_2H_5Br$	99.8
$n-C_3H_7Br$	101.6
$n-C_4H_9Br$	105.2

(4) No regularity seems to be detected among the energies of the carbon-halogen bond of normal, iso, secondary or tertiary compound of one halogen alkyl.

In connection with the study of the absorption in the ultraviolet region, it may be also worth while to compare the preceding results with the investigations of the Raman spectra and the infrared absorption spectra of these aliphatic organic compounds. According to Kohlrausch,[2] Harkins and Bowers,[3] the results of the investigation of the Raman spectra are in fairly good agreement with the preceding results obtained from the absorption spectra.

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[1] Y. Hukumoto, Sci. Rep. Tohoku **21**, 906 (1932); **22**, 13 and 870 (1933), etc.

[2] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (1932), 146, 215, etc.

[3] W. D. Harkins and H. E. Bowers, Phys. Rev. **38**, 1845 (1928); J. Am. Chem. Soc. **53**, 2425 (1931).

Quantized Molecules Formed of Excited Mercury Atoms and Methane Molecules

Oldenberg[1] has found that excited mercury and rare gas atoms will form complex structures due to polarization forces. Such molecules show diffuse bands on the long wave-length side of $\lambda = 2537$A. Methane molecule acts in this respect like a rare gas and we find similar bands when a mixture of methane gas (1 atm.) and mercury vapor

[1] O. Oldenberg, Zeits. f. Physik **47**, 195 (1928).

(20°C) is illuminated by a Hg(Ne) discharge tube. The following bands occur in fluorescence:

Band	(2536.7)	1	2	3	4
Center (cm^{-1})	39421	39330	39268	39213	39152

These diffuse bands are easily visible on the negatives, and the photomicrographs show them clearly. (See Fig. 1.)

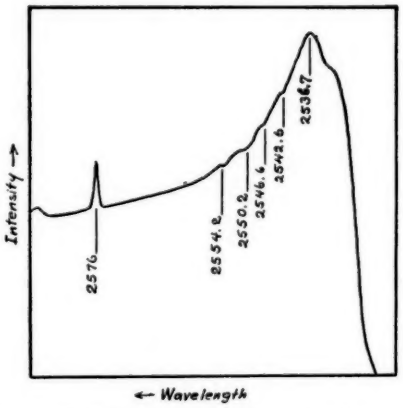

FIG. 1. Diffuse bands in CH_4—Hg mixtures near $\lambda = 2536.7$A.

These bands must be due to quantized states of a mercury complex with methane.[2] They cannot be due to Raman scattering from methane for the CH bond would produce a vibrational Raman line 3000 cm^{-1} from the exciting line and the rotational effect would be much closer to the exciting line ($\Delta\gamma_R = 10$ cm^{-1}).[3] Moreover the above bands are obtained in 30 minutes exposure. It has been shown that under the conditions of these experiments it is very unlikely that such bands are due to mercury molecules.[1]

The details of this research will be discussed in a future publication.

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[2] H. Kuhn and O. Oldenberg, Phys. Rev. **41**, 72 (1932).
[3] R. G. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34**, 582 (1929).

Raman Effect of Furane and Furfural

The following lines (cm^{-1}) were found with 4358A Hg line excitation using $NaNO_2$ filter:[1] *Furane:* 604, 735, 857, 990, 1055, 1139, 1381, 1486 due to the furane ring and 3165 due to the aromatic CH-bond. No line due to C=C is found. *Furfural:* 172, 497, 581, 929 and 1221 due to the alpha-substituted HOC group; 624, 758, 878, 1021, 1078, 1156, 1378, 1467 due to the furane ring. We find the C=C bond in the molecule at 1567 and the C=O bond at 1677. The aliphatic C—H bond (in HC=O) occurs at 2881 and the aromatic CH bond at 3129.

These results favor the centric formula for furane since no double bond is found. However, substitution has a great effect upon the structure of the ring itself. It is seen that alpha-substitution will cause the appearance of a double bond C=C within the ring. Similar findings have been reported by G. B. Monino (and co-workers[2]) in pyrrol.

The complete details will be published later.

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[1] A. H. Pfund, Phys. Rev. **42**, 581 (1932).
[2] G. B. Monino, *et al.*, Zeits. f. physik. Chemie **B22**, 21–44 (1933).

The Decomposition of Complex Molecules at High Pressures

The homogeneous thermal decomposition of gaseous paraldehyde to acetaldehyde has been investigated in this Laboratory from pressures of a few mm of Hg to about 18 atmospheres.[1, 2] (Above this pressure the liquid phase makes its appearance at temperatures where the rate is measurable.) It is believed that no other "simple" first order reaction[3] has been studied over as wide a range of pressure and that therefore, the results will be of interest. It is found that the velocity of the reaction slowly diminishes as the initial pressure is increased, the rate constant at 254°, for example, falling from 6×10^{-4} at several mm pressure to about 3×10^{-4} at 18 atmospheres. This result has been checked by different experimental methods and is therefore believed to be real. The following mechanism is suggested as a possible explanation which may apply generally to the first order decomposition of complex molecules.

If at an activating collision every possible energy dis-

[1] Coffin, Can. J. Research **7**, 75 (1932).
[2] Geddes and Coffin, Can. J. Research (In press).
[3] The decomposition of ethyl ether investigated by Newitt and Vernon (Proc. Roy. Soc. **A135**, 307 (1932)) up to 17 atmospheres pressure is "complex" in that it takes place by two different mechanisms each of which involves several intermediate steps.

tribution throughout the contributory degrees of freedom of a molecule is equally probable no effect of shortened mean free time (i.e., increased pressure) on reaction rate is to be expected since the particular distribution favorable to reaction is as probable as any other. If on the other hand the distributions most probable on collision are not coincident with those favorable to reaction a definite time interval must elapse between activation and decomposition due to the fact that different distributions follow one another at a finite rate. If such be the state of affairs therefore, the longer any one activated molecule is left alone the greater is the probability that it will react; that is to say the shorter the time between collisions (i.e., before deactivation) the smaller the chance of reaction. In other words increase of pressure may be expected to retard the reaction to an extent which is dependent upon the effectiveness with which the "vital" degree of freedom is protected and which will vary inversely as a linear function of the pressure.

This effect is to be expected particularly in the case of complex symmetrical molecules such as the paraldehydes[1, 2, 4] whose vital degrees of freedom lie well within the periphery presented by the rotating molecule to its colliding neighbors. Unfortunately in no case is it yet possible to estimate the necessary minimum time interval between the receipt and expenditure of activation energy and to compare its order of magnitude with that of the mean free time. Times of atomic relaxation however are known to be of the order of 10^{-8} sec.—an interval certainly longer than mean free times at pressures of one atmosphere or more—and vibrational excitation and its consequences might be expected to be more sluggish than electronic. Indeed the insulators suggested by O. K. Rice[5] (see also[6, 7]) will account for practically any time lag required.

Other reactions are being examined for this effect.

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[4] Coffin, Can. J. Research (In press).
[5] Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).
[6] Coffin, Can. J. Research **6**, 417 (1932).
[7] Coffin, Trans. Roy. Soc. Can. 1933 (In press).

The Equilibrium Between the Three Hydrogens

While studying the dependence of the equilibrium of the hydrogen-iodine reaction on the isotopic composition of the hydrogen,[1] it has been necessary to check the composition of the hydrogen by the mass-spectrographic method.[2] A sample of the hydrogen iodide used in this work was decomposed by allowing it to react at ordinary temperatures with mercury. Two other samples were the hydrogen produced by the decomposition of hydrogen iodide at 397°C and at 468°C. In determining the deuterium-protium ratio, the relative abundances of the three varieties of hydrogen molecules, H_2^2, H^1H^2 and H_2^1 were determined, thus permitting a determination of the equilibrium constants for the reaction,

$$H_2^1 + H_2^2 \rightleftarrows 2H^1H^2.$$

The equilibrium constant of this reaction has been calculated[1] and thus a check against theory can be secured.

Three samples were analyzed, check determinations being made on each. The results are summarized in Table I.

Table I.

Sample	T	Run	H_2^2	H^1H^2	H_2^1	K (obs.)	K (calc.)
5*A*	25°C	1	1.00	20.8	132	3.28	3.28
		2	1.00	21.2	137	3.28	
5*B*	397°C	1	1.00	13.9	46.0	4.20	3.73
		2	1.00	12.6	47.4	3.35	
6*B*	468°C	1	1.00	2.70	1.91	3.82	3.82
		2	1.00	2.68	1.96	3.68	

The numbers given under the headings H_2^2, H^1H^2, and H_2^1 give the relative abundances of the three molecules. At the time 5*B* was analyzed, the apparatus was fluctuating rather badly. The cause was later traced to variations in the magnetic field. When this trouble was remedied, much more reliable results were secured for 6*B*. In each case the observed equilibrium constant agrees closely with the calculated values. These are secured by interpolation from the tables previously published.

Samples 5*B* and 6*B* were prepared at the temperatures recorded in the table but remained in all glass containers at room temperatures for about twenty-one days before analysis. The fact that the equilibrium constants are those characteristic of the temperature of preparation shows that the exchange reaction does not take place rapidly, and thus that this reaction is similar to the exchange reaction between hydrogen and steam investigated by Crist and Dalin.[3] The time between preparation and analysis is not so long as that in the observations on liquid water and hydrogen by Oliphant,[4] and perhaps the method of analysis is not so sensitive.

[1] H. C. Urey and D. Rittenberg, J. Chem. Phys. **1**, 137 (1933).
[2] W. Bleakney, Phys. Rev. **41**, 32 (1932). H. S. Taylor, H. A. Gould and W. Bleakney, Phys. Rev. **43**, 496 (1933).
[3] R. H. Crist and G. A. Dalin, J. Chem. Phys. **1**, 677 (1933).
[4] M. L. Oliphant, Nature **132**, 675 (1933).

Also, the agreement between experiment and theory gives reasons for confidence in the mass-spectrographic method of analysis. This method depends on two assumptions. The first is the very reasonable one that the probability of ionization is the same for all three hydrogen molecules and these results are in agreement with that assumption. The second is that the equilibrium is not appreciably disturbed by the process of analysis, an assumption which has been investigated and shown to hold for the high rate of flow through the apparatus which was used here. The pressure and electron velocity were, of course, adjusted so that monatomic and triatomic ions were entirely negligible.

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